











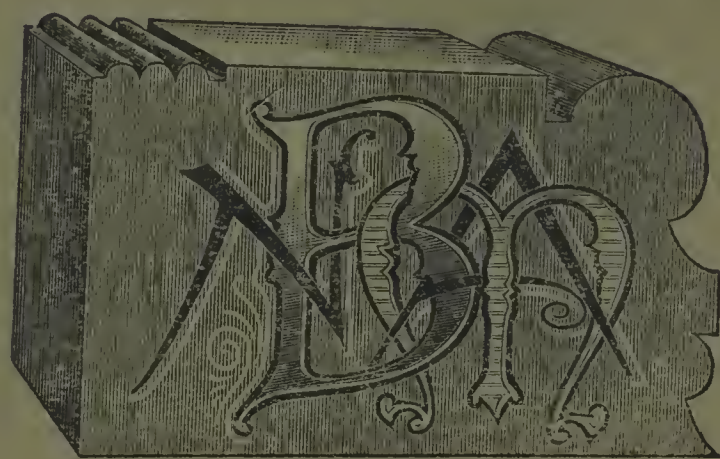








**The Status of Carbon, Iron,  
and Sulphur in Clays,  
DURING THE  
Various Stages of Burning.**



**Third Report of Committee on Technical Investigation.**

**Price \$1.00**





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—OF THE—

UNITED STATES OF AMERICA

# A Study of the Chemical Status of the Carbon, Iron, and Sulphur in Clays, during the various stages of Burning.

Being the Third Report of the Committee on  
Technical Investigation.

PERSONNEL OF THE COMMITTEE:

PROF. EDWARD ORTON, JR., Columbus, Ohio.....	Permanent Chairman
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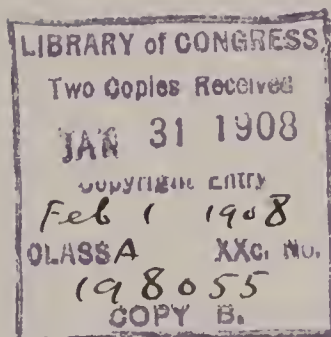
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Scholarship Appointee, 1904-1905.

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## LETTER OF TRANSMITTAL.

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THEODORE A. RANDALL, ESQ.,

Secretary National Brick Manufacturers' Association.

Dear Sir:—

It gives me pleasure to submit to you herewith the results of the investigation conducted by Mr. Homer H. Staley, B. Sc., and myself, on the status of the carbon, iron and sulphur compounds found in clay wares. The study is a chemical one, and is designed to shed light upon the behavior of the common, and in fact almost universally present impurities of clays, upon which we have at present very little direct evidence, and upon which much theorizing has been done with but little basis of facts for support.

In this investigation into the intimate chemical causes of the familiar phenomena which have been heretofore observed and described, some results have been obtained which are of importance, in that they show that the theories thus far advanced are in some respects true and in others entirely wide of the mark. While the work is by no means complete, it constitutes at least a clear step forward.

Very respectfully submitted,

EDWARD ORTON, JR.,

*Chairman of the Committee on Technical Investigation.*

Ohio State University,

Columbus, Ohio,

January, 1908.





## PREFACE.

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This volume is the product of the seventh year's work of the scholarship provided by the National Brick Manufacturers' Association in the Ohio State University. It was undertaken in September, 1904, and finished in July, 1905, except as to preparation for publication, which for various causes has been delayed until the present time.

The work undertaken is the direct continuation of or outgrowth from the work done in the preceding year, 1903-04, and which was published as the Second Report of the Committee on Technical Investigation, in 1905. This report dealt with the behavior of carbon as an ingredient in clays, and developed by a long series of synthetic mixtures and by various heat treatments of natural clays, a fairly complete demonstration of the behavior of carbon in clays and its effects on the iron during the burning process. The work did not, however, discover the intimate chemical cause of these various characteristic behaviors of clays impregnated with carbon. It developed the relationship of carbon to the various physical results or defects of the burning process, but did not disclose the train of chemical reactions which were responsible therefor.

But, like most other investigations, this one led directly to others. There seemed clear indications that sulphur was entitled to be considered jointly with carbon as the cause of some of these phenomena, and that the precise mode of operation of both on the iron of the clay during vitrification and fusion was yet to be worked out. The work was undertaken by Mr. Homer H. Staley, the scholarship appointee for that year, with great vigor and interest, and was carried forward during the year without more than general supervision and mapping out of the field of investigation. Mr. Staley deserves much credit for the way in which he handled the problem, and reduced his data.

This work has by no means completed what needs to be done along this phase of the subject, for it is simply a study of what happens in *one* clay during its various stages of proper and improper firing.

There is need of much other similar work being undertaken, because it may well be doubted whether the particular mineral aggregation of the clay studied is sufficiently typical to prove the case for other clays of different age and geological history. In particular, such a research ought to be undertaken on two or three synthetic mixtures, in which the composition could be controlled by using the various inert and active clay forming minerals in different proportions. It is hoped that other observers may undertake this problem, as this committee has now given as much attention to it as can properly be allotted to it from among the many other interests pressing for consideration.

EDWARD ORTON, JR., E. M.,  
*Chairman of the Committee.*

# A STUDY OF THE CHEMICAL STATUS OF THE CARBON, IRON AND SULPHUR IN CLAYS DURING THE VARIOUS STAGES OF BURNING.

BY

EDWARD ORTON, JR., F. M., AND HOMER H. STALEY, B. SC.

## HISTORICAL.

In the preceding Bulletin of this series\* the influence of carbon upon the burning behavior of clays was exploited with some care, and a fairly successful effort was made to learn the order of events under the various proper and improper methods of conducting the burning process. These sequences of cause and effect were investigated in their physical aspect chiefly, and while certain chemical hypotheses were necessarily used in picturing what was taking place in a burning clay, the investigation did not proceed rigorously to the proof that the result attained was really due to the postulated cause.

When the physical result attained was in agreement with what the chemical hypotheses led us to expect, it was accepted as evidence still further strengthening the hypothesis in question, though it might be really due to a concurrent cause which had not been clearly differentiated.

Seeger early did important work in this field as in most other phases of ceramic technology. In a number of papers†, he showed that both ferric and ferrous iron coexisted in most brick; that the ferrous oxide was never wholly oxidized into ferric, even after long continued treatment with hot air; that a considerable quantity of ferrous oxide may not appreciably affect the color of the clay, if the ferric oxide largely predominates; that if the ferrous oxide becomes as great or nearly as great as the ferric, the color is modified, and that ferrous colors are green, gray, black, or blue,

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\*The Influence of Carbon in the Burning of Claywares. Second Report on Committee on Technical Investigation. By Edward Orton, Jr., F. M. and Carl H. Griffin. Pub. T. A. Randall & Co., Indianapolis, Ind., 1905. 68 pp.

†See Bibliography following.



according to the clay, its density, its stage of deoxidation; that complete deoxidation to ferrous iron, with no ferric, is as rare as the reverse case, and many other points.

While a study of Seger's writings shows that he has considered deeply and presented data upon almost every phase of the status of iron in clays, there still remains uncertainty concerning a number of very important points. Among these, the two following may be mentioned:

(a) Does a red burning clay in undergoing fusion necessarily suffer a change of the ferric to ferrous state, i. e., is the darkening in color which generally accompanies fusion necessarily a sign of the formation of ferrous oxide?

(b) Does ferrous oxide really reduce fusion temperatures or not, i. e., is a ferrous silicate *per se* more fusible than a ferric silicate of the same constitution in other respects?

An effort to get at answers to these points was made in the conclusion of the above mentioned report (No. 2). The evidence, though not conclusive, has some value, and for the sake of continuity between the preceding year's work and the present, this data is here reproduced in full:

"Upon the completion of the experimental work to determine the influence of various factors upon the rate of carbon expulsion, a series of chemical analyses were engaged in to verify the conditions of the iron which have been assumed as existing in the normal and in the black-cored portions of clay-wares. Ten vitrified commercial clay products, all showing this phenomenon to a more or less marked degree, were selected for this investigation. From each of these, two samples were prepared, the one designated as A in the table of analyses, from the exterior portion of the ware, the other, marked B, from the interior.

**Samples.**—A description of the products from which these samples were taken, and the extent to which they have been affected by this reaction, is given as follows:

1. A stiff mud brick made from a low grade fireclay and burned in a test kiln at the Ohio State University. This sample shows a typical black core reaction, being composed of a comparatively thin band of pinkish color, surrounding a black core in which the structure has become more or less vesicular.

2. A dry press face brick composed of a No. 2 fireclay containing one-half per cent. of concretionary iron in the ferrous condition, manufactured at Canandaigua, N. Y. This sample is flashed on the exterior, showing numerous black

spots of iron slag upon a field of a warm brown color. The interior is light grey with a black center in which no swelling is evident.

3. A piece of drain tile from a plant near Ottawa, Ohio, made from an alluvial clay of a thoroughly oxidized character. Notwithstanding the fact that the iron in this clay was originally in the ferric condition, this specimen shows as good an illustration of the black-coring reaction could be found. The exterior of the tile is of a fine red color, penetrating to a depth of one-eighth of an inch, while the interior shows a black band three-fourths of an inch in width on a cross-section one inch in diameter. In ordinary practice, this clay would probably give no indication of this reaction, the trouble in this case having arisen from an unusually short firing period (twenty-four hours from lighting kiln to bright redheat).

4. A piece of Wassall block, made from an ordinary shale of Devonian age, occurring near Glouster, Ohio. This sample shows an extremely thin reddish film upon the exterior, the interior color being black, with a dark red core, showing that brick had once been perfectly oxidized. This brick has evidently been subjected to a heavy reduction, at the close of the burn, which in some places has penetrated to a depth of one inch, the surface color being due to reoxidation in cooling.

5. A dry press test block, made by W. D. Richardson, of Columbus, Ohio, and burned in a small up draft gas kiln. The clay used by him in this experiment was prepared by passing through fine screens, thus giving a finished brick of an exceedingly dense structure. This specimen shows a good red color, showing that it has either been reduced from a previously ferric condition or has failed to oxidize by contact of flame. This is not a typical black-core reaction.

6. A test piece of Haydenville fireclay, prepared in a wet way by passing through a 150-mesh screen, showing a thin oxidized film of a greenish grey cast, surrounding a bluish-black interior in which swelling has begun.

7. A piece of ordinary shale sewer pipe from North Columbus, Ohio. This sample shows a typical case of black-coring, the unoxidized portion, however, not being of sufficient size to cause swelling.

8. A red-burning paving brick showing practically the same phenomenon as sample No. 4. The brick has at one time been thoroughly oxidized, but the color of the exterior has been changed to a greenish-black by a subsequent reduction.

9. An ordinary shale paving block which has reached vitrification without having first been thoroughly oxidized. The exterior of this brick is of a normal red color, while the interior is composed of a mass of spongy black slag.

10—A. A dry press floor tile from the plant of the Mosaic



Tile Company, of Zanesville, Ohio. This sample is hard-burnt, being practically non-absorbent, and has a fine red color, which indicates perfect oxidation.

10—B. A piece of similar tile, composed of the same material. This sample had been fired to a higher temperature than the preceding one, but shows the same fine red color on the surface. The interior, however, is evidently suffering from the bluestoning reaction, as is shown by the appearance of mottled-black colorations irregularly disposed through the mass.

10—C. This sample represents the same material over-fired. It shows a thin film of a greyish-brown caste on the surface, the interior being of a bluish-black color, and showing an extreme case of bluestoning. No red color is left.

The first point, however, which seems to demand explanation is, whether any carbon, as such, exists in the clay after vitrification, or whether the black coloration, known as black core, is due entirely to the presence of iron as the ferrous oxide. In the *Thonindustrie Zeitung*\* the statement is made that black colorations in the interior of clay wares are due to ferrous oxide, derived from ferric oxide through the agency of organic matter present in the clay. Hopwood and Jackson, of the English Ceramic Society, state that this same phenomenon is due principally to the presence of free carbonaceous matter in the clay, which, by reason of an insufficient air supply, has been given no opportunity for oxidation, but that the effect of this agent is modified to a greater or less extent by ferrous oxide, ferroso-ferric oxide, and occasionally by sulphide of iron.†

**Carbon Determination.**—In the expectation of finding that the black color in the affected parts of these samples was due, in part at least, to the presence of free carbon, analyses for this substance were made in the laboratory of Prof. N. W. Lord, of the Ohio State University. These determinations were made by previously boiling the powdered samples in HCl to expel CO<sub>2</sub>, then igniting to a good red heat in an atmosphere of pure O, and determining the amount of CO<sub>2</sub> evolved, gravimetrically, by absorption in a weighed amount of caustic potash.

In none of these samples was any important amount of carbon found, the highest percentage shown in any case being well within the possible limits of error of the analysis. It is, of course, possible that had the silicate structure of samples been unlocked by digesting with hydrofluoric acid previous to their ignition, some carbon might have been found, but this is only a remote possibility, suggested by the results obtained by

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\*No. 90—Page 1,432, 1903.

†Trans. Eng. Cer. S., Vol. II, Pages 100-107.

Hopwood and Jackson, the truth of which can only be demonstrated by further experiment.

The samples analyzed by Professor Lord showed after ignition a decided transition in color from the bluish black to a red-brown tint, which, in the absence of carbon, indicates that the oxidation of the iron from the ferrous to the ferric condition has been responsible for the change.

**Probable Condition of the Carbon.**—It is probable that the carbon still remaining in the clay at the beginning of vitrification is converted into carbon monoxide or carbon dioxide by a reduction of the iron, and is retained in the mass of the clay under pressure. If the temperature is not increased beyond that point, these gases will give no indication of their presence, but will gradually filter out through the almost solid mass. But, on the other hand, if the heat be raised to a point at which the clay begins to soften, the increased pressure of the gases would cause the softened mass to swell and expand. The gases may or may not escape, depending on the degree of fluidity reached. Since the samples had been pulverized and boiled with HCl to expel all gases before ignition, the above theory is a plausible explanation of the absence of carbon as shown by these analyses, and whether it will finally be accepted or rejected, will depend upon future work to be carried out along the same general lines.

**Condition of the Iron.**—The next point to be considered was the condition of the iron in the normal and blackened portions of these same samples, determinations being made of the percentage of ferric and ferrous iron in each. The results of these analyses have been set down in the accompanying table.



TABLE NO. 1.

Sample No.	Percent FeO.	Percent Fe <sub>2</sub> O <sub>3</sub> .	Total Iron as Fe <sub>2</sub> O <sub>3</sub> .	CHECK DETERMINATIONS.					
				On FeO.			On Total Iron as Fe <sub>2</sub> O <sub>3</sub> .		
				1	2	3	1	2	3
1-A .....	0.95	4.95	.....	0.86	0.90	0.95	5.95	.....	.....
1-B .....	5.27	0.15	6.00	5.18	5.27	.....	6.00	.....	.....
2-A .....	1.13	4.15	.....	1.13	.....	.....	.....	*5.72	.....
2-B .....	4.73	0.20	5.45	4.73	4.73	.....	5.40	5.45	.....
3-A .....	0.45	6.20	.....	4.55	4.55	.....	.....	.....	.....
3-B .....	5.90	0.16	6.70	5.72	5.81	5.90	6.60	6.70	.....
4-A .....	4.73	1.15	.....	4.68	4.73	.....	.....	.....	.....
4-B .....	0.86	5.45	6.40	0.90	0.86	.....	6.40	.....	.....
5-A .....	3.74	2.25	.....	3.47	3.74	.....	.....	.....	.....
5-B .....	0.77	5.55	6.40	0.77	.....	.....	6.10	6.40	.....
6-A .....	1.49	2.15	.....	1.35	1.49	.....	3.80	.....	.....
6-B .....	3.02	0.45	3.80	2.88	2.84	3.02	3.80	*3.71	.....
7-A .....	1.04	6.35	.....	1.04	1.04	.....	.....	.....	.....
7-B .....	5.45	1.45	7.50	5.45	.....	.....	7.50	.....	.....
8-A .....	4.28	2.95	.....	3.92	4.28	.....	.....	.....	.....
8-B .....	0.81	6.81	7.70	0.81	0.81	.....	7.70	.....	.....
9-A .....	0.63	6.51	.....	0.63	0.63	.....	.....	.....	.....
9-B .....	5.63	0.95	7.20	5.54	5.63	.....	7.20	.....	.....
10-A .....	0.77	6.45	7.30	0.77	.....	.....	6.40	7.30	.....
10-B .....	1.22	5.95	7.30	1.22	1.22	.....	7.30	.....	.....
10-C .....	2.12	5.05	7.40	1.85	2.12	.....	7.60	7.40	7.40

\*By the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> method.

In general the above results show that the condition of the iron existing in the black, discolored portions of these samples is chiefly ferrous, and that in the red, normal portions, the ferric predominates. A most notable exception to this rule occurs in the case of Sample 10-C, which, it will be remembered, is a dry-press floor tile, suffering from an exaggerated case of bluestoning, and which upon fracture shows black from surface to surface. Judging by the results obtained in the preceding analyses we would expect to find that the iron was largely in the ferrous or black condition, and that the percentage of ferric iron was correspondingly small. As a matter of fact, however, the results show that just the reverse is true, and that the proportion of ferric iron to ferrous is approximately as 2.4 to 1.

It will be noticed that in those cases in which the black colorations have been formed on the exterior of the ware by the flashing or reduction of a previously oxidized portion, as in samples 4, 5, and 8, the percentage of ferric iron is relatively higher than in those formed by a typical black-core reaction. Sample 10-C is closely associated with this latter group of phenomena, in the origin of its present condition, which has been brought about by the reduction of a previously oxidized body. This, however, is as far as the relation extends, as the agents by which the reduction was produced are very widely different. In this case, the tile was subjected to a temperature too high to develop its best properties, sufficient of the iron thus being reduced to mask the red color of the ferric oxide and give to the whole mass a bluish-black appearance. This phenomenon represents the first step in the process of fusion, and it is probable that if the heat had been maintained at the highest temperature reached in the burning of this tile, for a length of time sufficient to have completely reduced the iron, this reaction would have taken place.

The result of these analyses has been to show that in the black, discolored portions of the samples, the iron is largely in the ferrous condition, while in the red, normal portions, the iron occurs principally as the ferric oxide. They also indicate that the coloring power of ferrous oxide is in itself sufficient in intensity to produce dark colorations, **even in the entire absence of carbon**, and that while they have not proven conclusively that there is no carbon present in these black cores after the clay has been vitrified, the evidence strongly favors such a conclusion."

Other evidence bearing on this same question was published by Mr. George C. Matson in the *Clayworker* for July, 1904, as a result of work done under Dr. H. Ries, at Cornell University.

"At the suggestion of Professor H. Ries, the writer undertook a series of experiments to determine whether the iron in clays returned to the ferrous condition as the clay was burned to viscosity in an oxidizing atmosphere. The results are given in the accompanying Table of Analysis. (See opposite page.)

"The clays were first molded into small bricks and then burned in a gas furnace, care being taken to raise the temperature slowly, and to keep the atmosphere of the furnace oxidizing. As soon as the burning was finished, the burned clay was covered with powdered feldspar or kaolin to prevent oxidation of the iron while cooling. The material for analysis was taken from the outside of the brick.

"The increase in the percentage of iron in the burned clay was due to the expulsion of water and other volatile substances in burning. All the analyses showed a decrease in the percentage of ferrous iron, and this taken in connection with the increase in the percentage of the total iron shows that the ferrous iron tends to change to ferric iron, even when the clay becomes viscous. However, with one exception (the clay from Amenia, N. Y.) there was ferrous iron present, which would indicate that the oxidation of the iron in the interior of the bricks was not complete; probably because the oxygen of the air did not penetrate to the interior very readily. Nevertheless, the results show that some oxidation took place even there. From the analyses, it would appear that the iron does not return to the ferrous condition except when burned in a reducing atmosphere.

"While this rule holds true for ordinary clays, it might not be true for a clay containing a large percentage of carbonaceous matter, which would tend to reduce the iron to a low state of oxidation unless the temperature was raised slowly enough to drive off the carbonaceous matter. Moreover, in the case of clays burned at a very high temperature, it may be impossible to maintain an oxidizing atmosphere in the furnace; and hence the iron will naturally be reduced."

The evidence of this work from various sources shows:

1st. That carbon is ascribed as the cause of the black colorations in improperly fired clay wares, but that the evidence so far available throws much doubt on this source as an important cause.

2nd. That the presence of iron in the ferrous condition is ascribed as the cause of black colorations in the center of either improperly burnt clay wares, or on the exterior of clay wares which are either reduced by smoky firing at high temperatures, or even by mere over-heating in oxidizing atmospheres. The



TABLE OF ANALYSIS.

1	2	3	4	5	6	7	8
Clay*	Condition	Color and Texture	Temp. Cone—F. C.	% Total Iron	% Ferrous Iron	% Ferric Iron	% Total Iron still in Ferrous Condition
Smith Landing, N. Y . . . .	Raw	. . . . .	. . . . .	7.307	2.550	4.817	34.60
“ “ “ . . . .	Burned	Melted to red, vesicular mass	8-2354-1290	10.490	1.263	9.711	12.18
“ “ “ . . . .	Burned	Red porous	3-2174-1190	10.364	1.779	9.101	16.90
Newfield, N. Y . . . . .	Raw	. . . . .	. . . . .	4.905	2.697	2.308	54.90
“ “ “ . . . . .	Burned	Melted to yellow vesicular mass	8-2354-1290	6.540	1.190	4.350	18.10
“ “ “ . . . . .	Burned	Yellow porous	3-2174-1190	6.020	1.799	4.221	28.80
“ “ “ . . . . .	Raw	. . . . .	. . . . .	8.371	2.398	6.973	29.00
“ “ “ . . . . .	Burned	Red, slightly porous	3-2174-1190	10.464	1.245	9.219	11.90
“ “ “ . . . . .	Burned	Red, very porous	5-2246-1230	13.080	1.090	11.990	8.30
Amenia, N. Y . . . . .	Raw	. . . . .	. . . . .	3.139	. . . . .	3.139	. . . . .
“ “ “ . . . . .	Burned	Red, slightly porous	5-2246-1230	4.185	. . . . .	4.185	. . . . .
Magnetite and Feldspar	Raw	. . . . .	. . . . .	34.404	12.271	22.133	35.60
“ “ “ . . . . .	Burned	Black, very porous	10-2426-1330	46.679	1.640	45.035	3.50

\*In column 1, the name applies to the locality from which the clay was obtained. In column 4, the temperature, Seger's cones were used. The F. and C. equivalents are from the Report on the Clays of Michigan, by H. Ries. In columns 5, 6 and 7, the per cent. is based upon the total weight of the clay; in column 8, the per cent. is based upon the total iron.



evidence so far collected favors this view as the common and potent cause of black colorations.

3rd. That iron in the ferric condition may exist in predominating amount intermixed with that in the ferrous condition, without imparting a red or brown color to the clay ware.

4th. That sulphur exerts an influence in some ways comparable to that of carbon, and that its behavior, rates of oxidation, and effect on color, vesicular structure, etc., have yet to be demonstrated.

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(5) The Natural Colors and Discolorations of Light-Colored Bricks. Page 347.

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## II. THE INVESTIGATION

Toward the settlement of the actual status of these three chief impurities of clays, during the various stages of burning, the following work was undertaken:

1st. To produce a carefully graduated series of samples, all from one homogeneous batch of the same clay used in the preceding studies, viz., the Black or Huron Shale of Columbus, representing all stages of the process of proper and improper firing.

2nd. To determine by careful analyses the quantity and chemical condition of each of the three substances, carbon, sulphur and iron in each sample.

3rd. To discover by study of the results what the behavior of these three substances is in this clay during firing, and to make such deductions as to their probable influence in other clays as the data seems to justify.

The selection of the Huron Shale was made for several reasons:

1st. It is known to be among the worst clays which has been commercially used for any length of time as the basis of clay manufacture. It has supported clay industries for a period of fifteen or twenty years in one locality and less periods elsewhere,

but in all places it is recognized as being on the very border line of unsuitability, and its use is now at a lower ebb than at any time in forty years in central Ohio.

2nd. It contains all three elements whose behavior is to be studied, in considerable amounts, and in such natural forms as are common in other carbonaceous or sulphury clays, thus saving the need of preparing synthetic samples.

3rd. The supply was here cheap and easily renewable, and could therefore be studied at minimum expense.

The work of the investigations naturally falls into two divisions, as follows:

III. Producing the test-pieces, which should illustrate the desired range of chemical and physical conditions.

IV. Analyzing these test pieces for the amounts of the carbon, ferrous oxide, ferric oxide, total iron, sulphur existing as soluble sulphates and insoluble silicate or sulphide forms, and total sulphur, and drawing the conclusions from the data. These divisions will now be taken up in turn.

### III. PRODUCING THE TEST-PIECES.

*The Clay.* The North Columbus Shale is thus described in an earlier report, in which it was used:

“This is a typical shale of the carbonaceous variety which is obtained from an outcrop of Devonian age at North Columbus, Ohio. The face of the exposure which is being worked there is from fifteen to twenty feet in depth and shows alternating strata of black and blue. The black layers are generally thinner than the blue, comprising approximately one-third of the deposit, and owe their dark color to the presence of organic matter as albertite or pitch. This black portion is a hard bituminous shale, with low plasticity and high carbon content, while the blue variety is comparatively soft, lower in carbon, and readily slakes down to a plastic clay upon exposure. This wide variation in physical properties is not due to the presence of carbon per se, but to the asphaltic character in which it occurs, which is supposed to have originated from a slow destructive distillation of the spores of coniferous plants, deposited in the clay at the time of its formation. This shale contains 5 to 7 per cent. of iron, present chiefly as the carbonate, and occasional marcasite concretions, but there is also a small amount of ferric iron as is shown by analysis. Another factor with which the brickmaker has to contend is the presence of gypsum or sulphate of lime, which causes the brick to



scum badly in the burning. Anywhere along the face of the clay pit, where the shale has not been worked for some time, a white efflorescence of this salt is found.

Two analyses of this shale, made at different times and on different samples at the Ohio State University, are given below:

TABLE No. 2.

CONSTITUENTS	1*	2†
Silica .....	58.38	57.69
Alumina .....	20.89	20.05
Ferrous Oxide, FeO.....	.....	7.07
Ferric Oxide, Fe <sub>2</sub> O <sub>3</sub> .....	5.78	1.08
Lime .....	0.44	0.61
Magnesia .....	1.57	1.23
Potash .....	4.68	3.94
Soda .....	0.34	0.43
Loss on ignition, including Water, Carbon and CO <sub>2</sub> ..	7.53	8.24
Total.....	99.61	100.34

It will be noticed that in analysis No. 1, the iron is given as the ferric oxide, no ferrous iron being noted. The ordinary practice in analyzing clays has been to determine the total iron as Fe<sub>2</sub>O<sub>3</sub>, no account being taken of the condition of the iron in the original sample, hence the above result. Now, it is the custom among ceramic chemists to determine not only the total iron as in former years, but to note the distribution between the ferrous and ferric forms.

It will be noticed that in neither of these analyses was the sulphur determined, though of course it was partly included in the loss on ignition over the blast lamp.

#### *Preparation of the trial-pieces.*

The crude clay was ground in a small dry-pan and screened. The screenings were further ground in a large mortar until all had passed through a sieve of 16 meshes to the linear inch. The mass was then tempered in a pugmill with distilled water, up to the consistency required for stiff-mud bricks, and was then blanketed and allowed to stand for several days, in order that

\*Professor William McPherson, Analyst.

†Professor Albert V. Bleining, Analyst.



the water might become uniformly distributed and all hard grains have opportunity to soften if they would. Distilled water was used so that no iron salts or sulphates might be introduced into the clay with the water, as the ordinary hydrant water in Columbus contains noticeable amounts of both.

The tempered clay was finally wedged by hand, on a clean board, to expel inclosed air and obtain the best homogeneity. The use of a regular plaster wedging block was avoided for fear of the introduction of particles of  $\text{CaSO}_4$ . The samples were pressed in a hand power screw tile press, in which a dense uniform structure can be obtained without the structural defects ordinarily found in bricks where made by causing clay to flow through a die under pressure.

The size of the brickettes was  $4\frac{1}{4} \times 4\frac{1}{4} \times 2\frac{1}{2}$  in the green condition. They shrank moderately in drying, being about  $4 \times 4 \times 2\frac{5}{16}$  when dry. These brickettes were about equivalent to half brick in size, having the full cross-section of standard brick as to breadth and thickness, and only differing from them in length. They dried without cracking in the ordinary room temperature of the University laboratory.

*The Burning.* It was the intent in the burning process to produce three sets of brickettes, viz.:

*Burn A.* A set which should be fired rapidly through the oxidizing period, without affording any adequate time for oxidation, and then carried steadily, but at normal speed through the vitrification period.

If trials were drawn at stated intervals in such a heat treatment, and cooled rapidly and then broken, they would show a series of black-cored products, changing from the soft crumbly center bordered by a flesh pink crumbly exterior during oxidation, to a hard dense black center, bordered by hard dense red exterior during vitrification, and to a puffy scoriaceous black center during overfire, bordered by a red exterior of dense or at least less scoriaceous fracture, according to the degree of overfire. This series was designed to show the results of bad or hasty oxidation, good vitrification conditions, followed by overfire.

*Burn B.* A set which should be fired slowly until oxidation was complete at a low temperature, followed in turn by vitrification under good conditions, and finally by overfire. This series

was designed to represent normal or good burning, except it was to be allowed to go too far.

*Burn C.* A set which should be fired slowly until oxidation and vitrification were complete, when a period of heavy reducing treatment without increase of temperature would begin, followed by raise of temperature sufficient to cause overfire, still maintaining reducing conditions.

This series was designed to show the results of proper firing during the early portion of the burning, followed by improper conditions at the finish. This is a very common condition to find in burns of every kind of ceramic product.

These three heat treatments may be graphically illustrated by the following diagram:

Burn A	Burn B	Burn C
<b>Oxidation</b> Bad. Too rapid.	<b>Oxidation</b> Good. Slow as necessary.	<b>Oxidation</b> Good. Slow as necessary.
<b>Vitrification</b> Good. Oxidizing Conditions.	<b>Vitrification</b> Good. Oxidizing Conditions.	<b>Vitrification</b> Good at first. Turning to reducing towards end.
<b>Over-Fire</b> Good. Oxidizing Conditions.	<b>Over-Fire</b> Good. Oxidizing Conditions.	<b>Over-Fire</b> Bad. Heavily Reducing.

Figure 1. Comparison of the three heat treatments.

To attain these three sets of conditions with the least labor and delay, two kilns were used simultaneously. Both were small test-kilns, but one was larger than the other and will be known as the large kiln. The large kiln was a down draft, having but one fire box. From the fire box the gases pass up flues on either side of the chamber in which the ware is set, enter it through small holes in the side walls near the top, pass downwards through the ware chamber and out through openings in the floor of the ware chamber into a flue which empties into the stack. The ware chamber of the kiln measures 20 inches wide x 30 inches long x 80 inches high. As this space was too large for our purpose, it

was filled in at the top and bottom with a checker-work of burnt fire-brick. In the center, an open chamber was left among the fire-brick, which were placed loosely and without mortar, to facilitate the flow of gases through the test brick. With a little care in firing, it was possible to maintain continuously oxidizing conditions in this ware chamber.

The smaller kiln was an up-draft muffle. It has but one fire box, which is provided with a coking plate. The muffle is directly above the fire, but about two feet distant. It consists of a tight brick box, built of well-mortared fire-brick, supported on arches. Both sides, one end, and the top and bottom are exposed to the play of the flames and combustion gases. The other end contains the wicket and is necessarily left unexposed to the hot gases to facilitate drawing trials. The inside measurements of the muffle are 10 inches high by  $13\frac{1}{2}$  inches wide by 27 inches long. The interior of this muffle being sealed off from the combustion gases, it is possible to maintain quite exact control of the composition of the atmosphere in it.

The plan of the burning was to place all the trial pieces in the larger kiln, carry the temperature with reasonable speed up to about  $800^{\circ}\text{C}$ , and to hold it there under oxidizing conditions until trials withdrawn should show a sufficient zone of oxidized clay on the exterior, surrounding a large black core still heavily charged with carbon. When oxidation should have reached the desired point about one-third of the samples were to be removed and quickly transferred to the smaller or muffle kiln, which in the meantime was to be heated up to  $800^{\circ}\text{C}$ . In this kiln, the imperfectly oxidized brickettes were to be treated according to the program for Burn A. Meanwhile, the larger kiln was to be carried along at  $800^{\circ}\text{C}$  under favorable oxidizing conditions until the last of the carbon had disappeared from the center of the two-thirds of the brickettes still remaining in it. This was determined, of course, by drawing and breaking trials, until the oxidation was complete. When burn A was completed, and the last sample drawn, the muffle was cooled down to  $800^{\circ}\text{C}$  and a second lot of samples, now fully oxidized, were quickly transferred from the larger kiln to it. These were then treated according to the plans for Burn B. When Burn B was in turn complete and the trials all drawn, the muffle kiln was to be again cooled down to  $800^{\circ}\text{C}$ , and the final third of the brickettes was to



be transferred from the larger kiln, and treated according to the plans for Burn C.

The burning was carried out strictly according to this program. Forty samples were placed in the large down-draft kiln. Care was taken to separate them from the floor and each other by use of small spacers, set on edge. In this way, all sides of each brickette were almost equally exposed to the play of the gases. The thermocouple of a Le Chatelier pyrometer was placed directly in the midst of the samples, in order to get an exact record of the temperature.

The kiln was heated up with an abundant excess of air, as fast as was feasible without injuring the ware.

The time-temperature curve of both kilns and for all three heat treatments is shown in Figure 2:



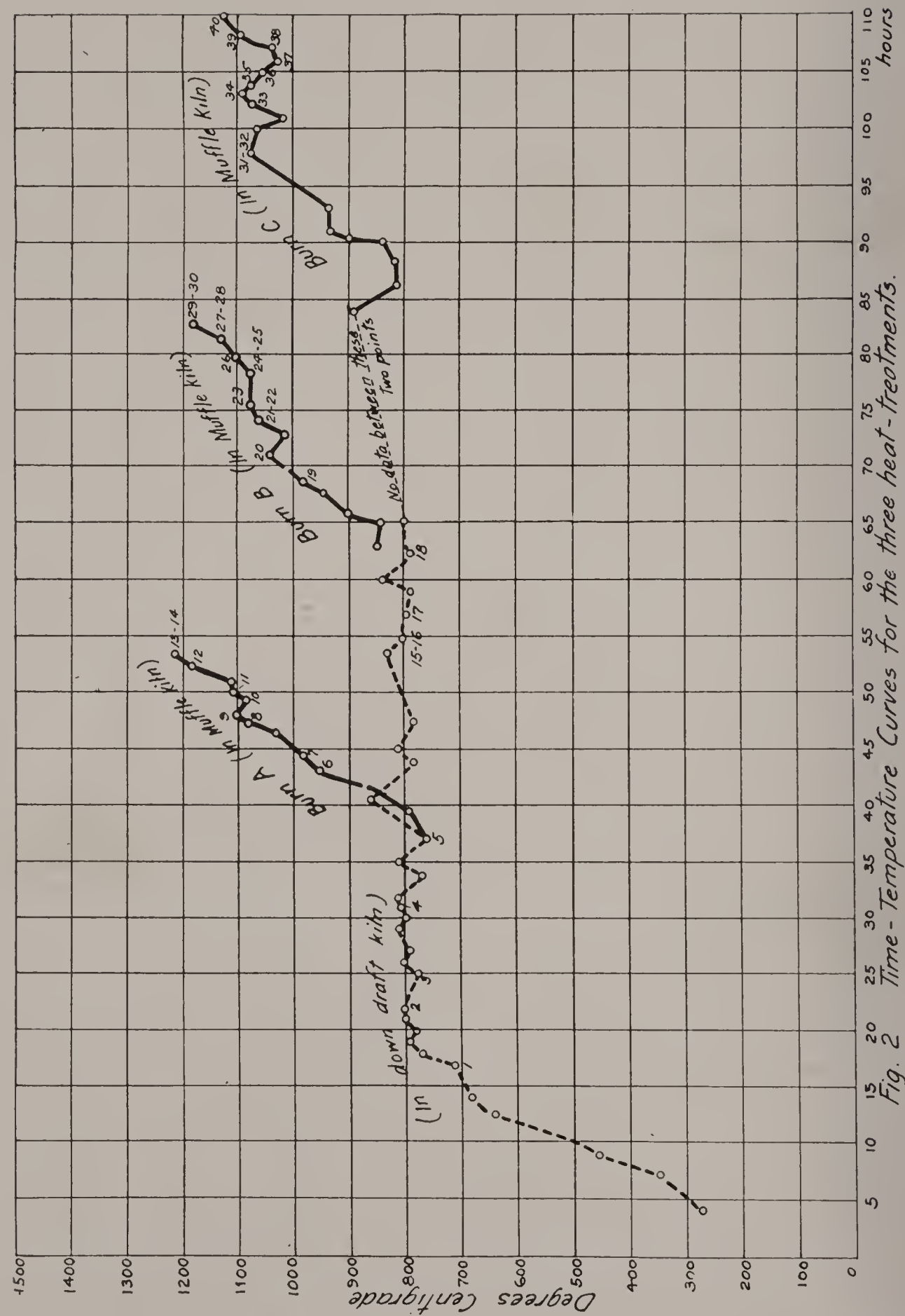


Fig. 2 Time - Temperature Curves for the three heat-treatments.

The dotted line indicates the progress of events in the down-draft muffle kiln, while the solid lines show the progress of the several burns after the brickettes had been transferred to the up-draft muffle kiln. The gaps between the starting points of the curves of Burn B were due to the failure to record observations promptly after making a transfer of brickettes from the first kiln to the second. The gap between the end of the dotted line curve, at the 65th hour, and the beginning of curve for Burn C, at the 83rd hour, was due to using the thermocouple exclusively in Burn B during this period. When the temperature of the down-draft kiln was taken, at the end of Burn B, it was found that it had crawled up to  $890^{\circ}\text{C}$ , and after transferring to the smaller kiln, the temperature was brought back to  $810^{\circ}\text{C}$  for a few hours before starting on the reducing burn. The temperature did not go as high in Burn C as in A and B, because the reduction caused the brickettes to slag equally at a lower temperature.

As can be seen from Figure 2, trial No 1 was drawn at the seventeenth hour of the burn, at a temperature of  $710^{\circ}\text{C}$ . It was cooled and broken across the center. This process was repeated throughout all the burns, trials being drawn at sufficiently short intervals to enable the operators to keep close watch on all the changes that were taking place in the ware, and thus secure samples at any desired stage of the burning process.  $800^{\circ}\text{C}$  was reached at the twenty-first hour of the burn, and the large kiln was then held at approximately that temperature, and under thoroughly oxidizing conditions, till the last brickettes had been drawn from it at the 83rd hour.

Trial No. 5, drawn at the thirty-seventh hour of the burn, showed that oxidation had proceeded fairly well into the bricks. At this point twelve samples were quickly transferred to the muffle kiln. Both kilns were at approximately  $800^{\circ}\text{C}$ . These constituted the samples for burn A, and the treatment they received was according to the program already described for that burn. The time temperature curve and indications of the points at which trials were drawn is shown.

Photographs of typical trial pieces from Burn A are shown in Figure 3.

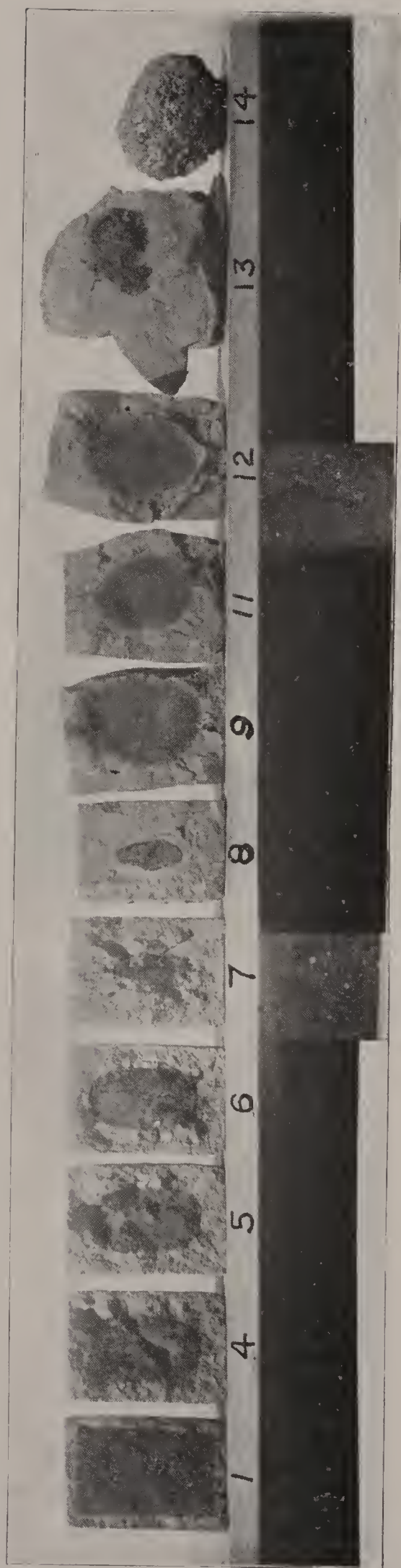


Figure 3. Samples illustrating the behavior of brickettes in Burn A, which were raised to vitrification temperature, without awaiting for complete oxidation to take place.



The following is a description of the heat pieces shown in each group:

Draw No. 1, taken at 17 hours after beginning of the burn. Temperature 710°C. Exterior oxidized layer one-quarter to three-eighths inch thick, pale pink color. Interior unoxidized core, dark, almost black, with sharply defined margin. Both portions soft and crumbly.

Draw No. 4, taken at 31 hours. Temperature 805°C. Exterior oxidized portion, one-half to five-eighths inch thick, brighter pink color. Interior core, lighter, grayer color and shades into exterior zone more gently. Both portions still soft.

Draw No. 5, taken at 37 hours, at time of transfer of brickettes from downdraft kiln to updraft muffle for the beginning of the special treatment. Temperature 760°C. Physical characteristics unchanged from draw No. 4, except slight decrease in size of the core.

Draw No. 7, taken at 44 hours. Temperature 980°C. Areas of outer oxidized zone and inner unoxidized core about as in No. 4, but edges of areas are more sharply defined. Color, outer zone, flesh-pink; inner core, grayish black. Hardness, both can be cut with knife, easily.

Draw No. 8, taken at 47½ hours. Temperature 1080°C. Outer zone three-quarters inch thick, inner core about 1 inch x 2½, oval. Color, fair red exterior, light bluish black core. Hardness, materially greater, core harder than exterior, but both can be cut.

Draw No. 9, taken at 48 hours. Temperature 1100° C. A marked physical change has taken place, more than commensurate with the change in time or temperature. Probably explained by uneven distribution of heat in the first or larger kiln. Shrinkage has set in strongly. Vitrification marked. Cannot cut either red outer zone or blue core. Area of latter considerably smaller, and margins definite. Body at its densest state.

Draw No. 10, taken at 49 hours. Temperature 1090°C. The shrinkage shown in draw 9 has been more than offset by the beginning of swelling. The central black core is much larger than No. 9, but this is not due to its expansion, at least not to any large degree. The core was larger when the advancing vitrification overtook it and prevented further oxidation. The core has swollen somewhat, however, and is microscopically vesicular. The outer red zone is still dense and not overfired, though very hard.

Draw No. 11, taken at 50 hours. Temperature 1105°C. The swelling of the core is becoming clearly evident. It has deformed the outer red zone, which is as yet not affected by overfire, and it has become so coarsely vesicular that the bubbles can be seen by the eye.



Draw No. 12, taken at 52½ hours. Temperature 1180°C. The process of swelling has progressed, and has now involved the exterior red zone as well. The black core is coarsely vesicular. The red exterior is finely vesicular.

Draw No. 13, taken at 53½ hours. Temperature 1210°C. A portion of the trial only is shown. The trial had swollen enormously and could no longer be broken squarely across, but broke into irregular sharp jagged masses, like slag or glass. The piece shown exposes the red vesicular sponge of the outer layer, and a small part of the still more vesicular spherical core.

Draw No. 14, taken after the muffle had cooled down to 800° preparatory to receiving its brickettes for Burn B. The temperature did not go above that of Draw 13, but was of somewhat longer duration. The sample represents the spherical black core only. It is a light scoriaceous cinder, which will float in water for hours. The exterior red vesicular mass has cracked away from the core, like the shell from a kernel. The red portion is not as coarsely bubbled as the black, but it is equally weak and worthless.

The only variation from the program was that between the forty-seventh and forty-ninth hours, after the bricks in the kiln had partially puffed up, the temperature was held uniform for two hours, to show the effect of heat-soaking. This burn was completed at the fifty-third hour, trial No. 14 being the last sample. The muffle kiln was then cooled down to the temperature of the large kiln, and prepared for Burn B.

As the samples in the large kiln were not thoroughly oxidized yet, they were still treated in the large kiln for ten hours, when the charge for Burn B was transferred at the sixty-first hour. This burn was then carried out strictly according to program. The time temperature curve with indications of the points at which trials were drawn is shown in Figure 2. Also, photographs of typical trial pieces of the burn are shown in Figure 4. This burn was completed at the eighty-second hour, No. 30 being the last trial-piece to be drawn.

Draws 1, 4, 5, 7, described under Figure 3.

Draw No. 17, taken at 57 hours. Temperature 790°C. The sample was still oxidizing in the downdraft kiln. No important change in physical condition since sample 5 was taken. A very small black core still existed, and the burn was carried on 5 hours longer, before transferring charge to updraft kiln for special treatment.

Draw No. 19, taken at 68½ hours. Temperature 980°C.

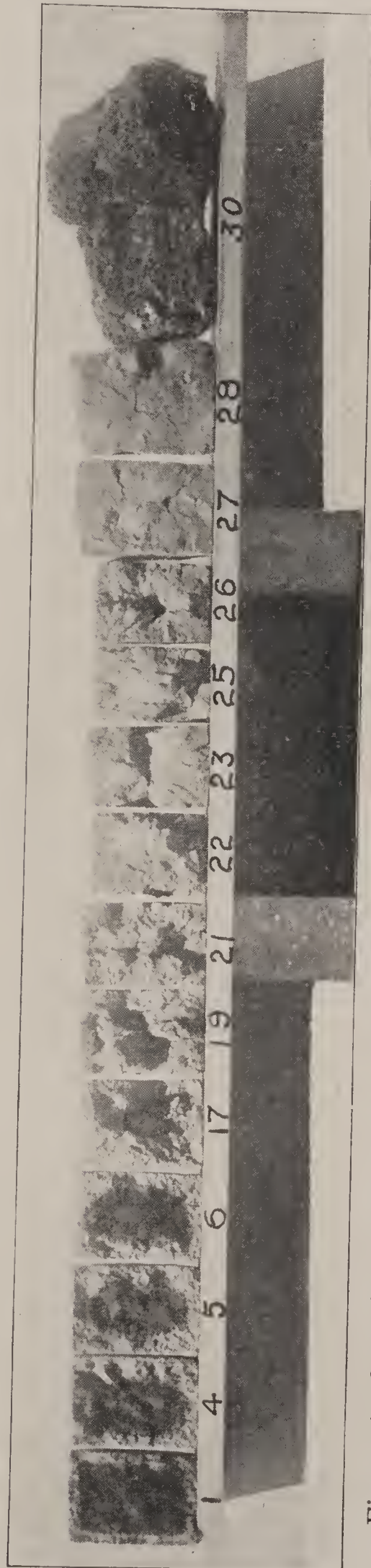


Figure 4. Samples illustrating the behavior of brickettes in Burn B, which were raised to vitrification under the best possible conditions, but were finally carried into overfire, under oxidizing conditions.

Just beginning to show a little hardening, but still cuts with knife, readily. Color uniform red. Shows a slight shrinkage.

Draw No. 21, taken at 74 hours. Temperature 1060°C. Much harder, but can still be cut a little. Shrinkage nearly complete. Fracture still granular. Color, good red throughout.

Draw No. 22, taken at 75 hours. Temperature 1070°C. Shrinkage complete. Fracture denser and less granular, but not fully vitrified. Color, good red throughout.

Draw No. 23, taken at 75½ hours. Temperature 1075°C. No change in volume or color. Fracture becoming smoother and less granular.

Draw No. 25, taken at 78 hours. Temperature 1075°C. No change in volume or color. Fracture smooth and glossy in most part. Cracks or lamination flaws beginning to open up in the mass. Past the best vitrification point.

Draw No. 26, taken at 79½ hours. Temperature 1100°C. Fracture smooth and glossy. Color, brown, uniform throughout. Cracks opening wider. Obviously deteriorating from over-fire. No change in volume as yet.

Draw No. 27, taken at 81 hours. Temperature 1125°C. The swelling greatest on the exterior half inch, where the fracture is fine grained vesicular. Interior still smooth and glossy except for flaws, and does not show vesicular structure yet. Color, dark brown-red.

Draw No. 28, taken at 81½ hours. Temperature 1125°C. Still further swelling. Vesicular structure worst and coarsest on exterior, but plainly visible clear through the mass. Cracks and flaws widening as the mass swells.

Draw No. 30, taken at 82½ hours. Temperature 1180°C. Body degenerated into a shapeless froth or sponge, which floats on water. Volume three or four times original size. Color, dark brownish red. Does not show any ferrous color or reduction.

The muffle kiln was then cooled down to about 800°C, and, in the eighty-fourth hour Burn C was started. This also was carried out according to program. Trial No. 34, drawn at one hundred and three hours, showed a good dense structure. Reduction treatment was then applied. The wicket of the muffle was opened and about one pound of bituminous coal in small lumps was thrown in. The wicket was then quickly closed. The muffle immediately became filled with dense black smoke. The temperature was kept uniform. More coal was thrown into the muffle an hour and a quarter later, and the muffle kept filled with dense black smoke. Trial No. 37, drawn at the one hundred and sixth hour, showed black or blue vitrification extending deep



into the brick, a small red spot being left in the center. The heat was then raised, the ware still being kept under reducing conditions. The burn was completed at the one hundred and tenth hour, trial No. 40 being allowed to cool in the kiln with the damper down and the fire gases passing out through the muffle to ensure final reduction. The time temperature curve of Burn C is shown in Figure 2. Photographs of the typical trial pieces are shown on Figure 5.



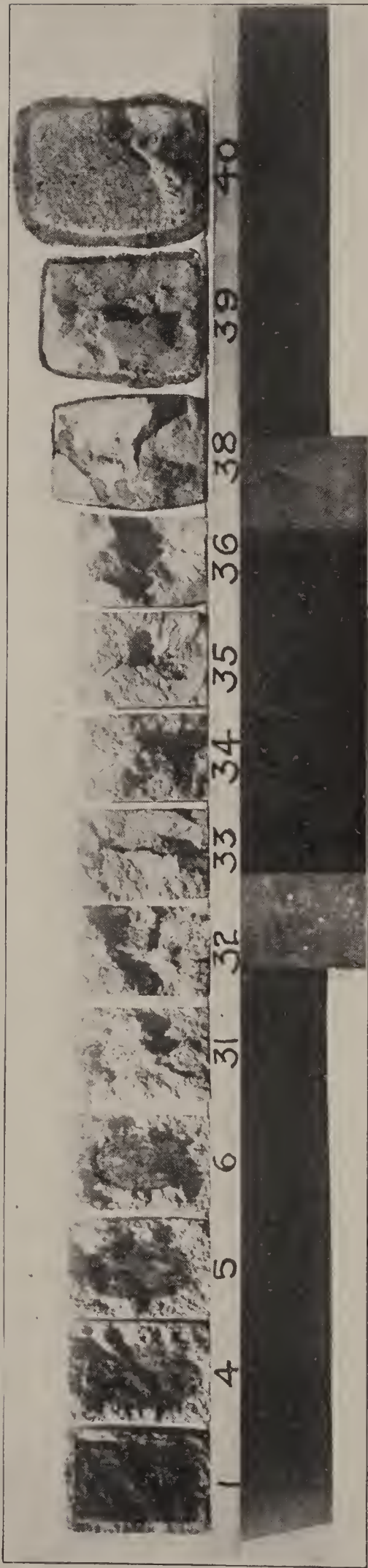


Figure 5. Samples illustrating the behavior of brickettes in Burn C, which were oxidized and vitrified in a normal manner, and were then subjected to heavy reduction and raise of temperature under reducing conditions.

Draws Nos. 1, 4, 5 and 7, described under Figure 3.

Draw No. 31, taken at 98 hours, at temperature 1080°C. The brickette had attained a fairly complete vitrification. Was too hard to cut, and of clean red color throughout. Shrinkage about complete. Reduction not yet begun.

Draw No. 32, taken at 98½ hours. Temperature 1080°C. The reducing treatment had begun, and a blue band had formed about ¼-inch deep on exterior of brick. Meanwhile, shrinkage had gone on still further, to completion.

Draw No. 33, taken at 102½ hours. Temperature 1075°C. The second reducing treatment had begun. Sample was blued deeply, but some normal red color still existed in the center. No vesicular structure as yet.

Draw No. 34, taken at 103 hours. Temperature 1090°C. Blueing process going on steadily. No swelling yet begun. Body dense. Glossy fracture.

Draw No. 35, taken at 104 hours. Temperature 1080°C. Brick beginning to show large cracks due to internal flaws and shrinkage defects. No swelling yet apparent. Body smooth and glossy fracture. Blue color on exterior.

Draw No. 36, taken at 105 hours. Temperature 1060°C. Vitrification very far advanced. Body breaks in smooth glossy fractures, very few grains apparent. Color blue on exterior. Swollen somewhat, chiefly by opening of flaws and cracks inside. Not vesicular, to the eye.

Draw No. 38, taken at 107½ hours. Temperature 1040°C. Swollen badly, beginning at outside and progressing inwards. Soundest body in center. Color blue, with a small red core.

Draw No. 39, taken at 108½ hours. Temperature 1100°C. Exterior, coarsely vesicular, and burnt to a cinder ¼-inch thick. Interior, vesicular, but in fine even texture. Cracks and flaws opened widely. Color blue throughout.

Draw No. 40, taken at 110 hours. Temperature 1130°C. Whole body very vesicular. Exterior notably worse than interior. Swelling has trebled volume of brickette. Color blue throughout.

A study of these three series of trial pieces shows conclusively that the practical understanding and control of the burning process for the clay had been worked out in the preceding year's work as detailed in the preceding report (second), for three types of structure were produced at will, viz.:

(a) The black-cored, swelled brickette, with red exterior.

(b) The red brickette, with good dense structure until overfired, and with vesicular structure proceeding from outside, inwards, when overfire set in, and with preservation of the red color throughout.

(c) The red brickette, with good dense structure, changed to a black cindery mass from outside, inwards, until on over heating, the whole mass was a vesicular sponge with black exterior and partially red interior.

The very fact that these three characteristic varieties of color and physical structure could be produced with certainty and on the first attempt, shows clearly that the practical control of the burning process can be secured by following the methods prescribed as the result of the preceding year's work, and to that extent it adds weight and authority to the opinions already announced in that place.

#### IV. THE CHEMICAL WORK.

*Sampling.* The number of samples secured in these various burns were so large that it was impossible in the time available to make analyses of all, nor did it seem that the comparatively small differences in degree between the changes in adjacent samples warranted the expense of separate chemical tests. Therefore the following samples were selected as types of the various stages of the processes represented, viz., the raw clay and draw trials 1, 4, 7, 9, 14, 21, 22, 25, 28, 29 and 37.

The raw clay and draw trial No. 14 consisted of one kind of material only, and were therefore prepared by pulverizing through a 100 mesh screen, mixing thoroughly, and putting away in stoppered glass bottles.

All of the other samples represented two sets of conditions or two kinds of structure, and were therefore carefully broken, and the requisite quantity of both the inner and outer portions were taken separately, and two samples prepared. The distinguishing of the inner and outer portions usually was very easy by observing the colors. In other cases, the brickettes were broken, piece by piece, and the material divided into outer and inner layers as fast as broken. All samples were carefully pulverized and put up in stoppered bottles.

The nature and peculiarity of each test piece can be easily found by consulting the description of the draw trials, under figures 3, 4 and 5, and can be still better appreciated from a study of the photographs of the more characteristic ones, which are printed herewith.





Figure 6. Showing cross section of Draw trial No. 1, drawn at 710°C after 17 hours in the kiln.

The carbon has been burned out to a depth of about 5-16 inch, leaving the surface flesh pink in color. The core is very dark. The texture of both portions is very soft and crumbly.

ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Outer Oxidized Portion.....		0.31	5.02	0.94
Interior Unoxidized Portion.....	2.31	4.56	0.67	2.40





Figure 7. Showing cross-section of Draw trial No. 4, drawn at 805°C, after 31 hours.

The carbon has been burnt out to a depth of  $\frac{1}{2}$  or  $\frac{5}{8}$  inch. The outer portion is pink in color. The black core is much lighter and grayer than Fig. 6. Texture of both portions is still soft.

ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Outer Oxidized Portion . . . . .	.....	0.36	5.23	0.68
Interior Unoxidized Portion . . . . .	1.173	5.49	0.62	2.28



Figure 8. Showing cross-section of Draw trial No. 7, drawn at 980°C, after 44 hours.

The carbon is burnt out to a depth of  $\frac{3}{4}$  or  $\frac{7}{8}$  inch, leaving the surface a flesh-pink color. The core is grayish black. The texture is much harder, but can still be cut with a knife. The shadows in the picture obscure a considerable part of the core, which can be discerned only in its upper half.

#### ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Outer Oxidized Portion.....	.....	0.56	5.33	0.53
Interior Unoxidized Portion.....	0.151	5.34	0.51	2.15



Figure 9. Showing cross-section of Draw trial No. 8, drawn at  $1080^{\circ}\text{C}$ , after  $47\frac{1}{2}$  hours.

The carbon was tested in the black core but none was found. The exterior of the brick is a fair red color. The center is light bluish black. A marginal ring of a bright, different shade of red from the exterior encircles the black core. The exterior is fairly hard but has not lost its granular appearance. The red ring and the black area are more vitrified and break into a smoother fracture than the exterior, as can be seen. Not analyzed for other ingredients than carbon.





Figure 10. Showing cross-section of Draw trial No. 9, drawn at 1100°C, after 48 hours.

The size of the core and its relatively advanced degree of vitrification was probably not due to sudden changes occurring in the short period since Draw No. 8. It was probably due to irregularities of distribution of the air currents and possibly of temperature in the first kiln, by which some of the brickettes were further advanced when they were transferred to the second kiln for special treatment.

This brickette has passed beyond the most favorable stage of vitrification; the exterior is only a little spongy, but the center has swelled and deformed the exterior. The center is visibly spongy. The brick is hard and cannot be cut.

#### ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Outer Oxidized Portion . . . . .	0	0.95	5.90	0.32
Interior Unoxidized Portion . . . . .	0	5.31	0.36	2.06





Figure 11. Showing spherical core of Draw trial No. 14, after the red exterior shell had been cracked loose and removed.

Taken after the kiln had cooled down to  $800^{\circ}$  preparatory to Burn B. The trial had not endured any temperature higher than No. 13, which was drawn at  $1210^{\circ}\text{C}$ , but it had stood a slightly longer exposure to heat.

Both exterior and interior are light scoriaceous cinders.

#### ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Inner Unoxidized Portion.....	0	6.15	0	1.34
Outer Oxidized Portion, not tested .....	.....	.....	.....	.....



Figure 12. Showing cross-section of Draw trial No. 21, drawn at 1060°C, after 74 hours.

The trial was fully oxidized, there being but one uniform red color throughout. Sample was getting hard but could still be cut with a knife.

#### ANALYSIS.

Ferrous Oxide .....	0.57
Ferric Oxide .....	5.43
Total Sulphur .....	0.29



Figure 13. Showing cross-section of Draw trial No. 25, drawn at 1075°C, after 78 hours.

The trial was smooth and glossy in fracture for the most part. The color was a good red throughout. Cracks or laminations are beginning to open in the mass, indicating the beginning of over-fire. No swelling as yet.

#### ANALYSIS.

Ferrous Oxide .....	0.61
Ferric Oxide .....	5.54
Total Sulphur .....	0.23





Figure 14. Showing cross-section of Draw trial No. 28, drawn at 1125°C, after 81½ hours.

Notable swelling has taken place. The vesicular structure is worse on the exterior and least in the center, but can be observed all through the mass. Flaws and laminations spreading open widely.

#### ANALYSIS.

Ferrous Oxide .....	0.61
Ferric Oxide .....	5.54
Total Sulphur .....	0.22



Figure No. 15. Showing piece of Draw Trial No. 30, Burn B. This was a frothy cinder, light enough to float on water, but it was red in color, showing that even this high degree of fusion had not affected the status of the ferric iron. This sample shows the extreme point of breakdown of a ferrugineous clay, which had been properly oxidized and properly vitrified, and then subjected to normal over-fire. The expulsion of sulphuric acid is thought to be the cause of the highly spongy structure. This sample was not analyzed, but No. 29, showing almost identical physical structure, contained 0.17 total sulphur, while No. 28, taken just before the heavy swelling began, showed 0.22 sulphur.



Figure 16. Showing cross-section of Draw trial No. 37, drawn at 1030°C, after 106 hours.

Vitrification complete. Body breaks in smooth glossy fractures. Color is blue or black externally, with small red interior spot, not yet reduced. The rough granular area seen in the cut is a “dry spot,” or a break along a pre-existing flaw in the brick, and does not mean that the real texture of the brick is granular at all. From this trial, swelling developed rapidly as the temperature went up.

ANALYSIS.

	Carbon	Ferrous Oxide	Ferric Oxide	Total Sulphur
Exterior Reduced Portion.....	0	6.26	0.35	0.26
Interior Red Portion. ....	0	0.11	6.55	0.21





Figure 17. Showing a cross-section of Draw trial No. 39, drawn at 1100°C, after 108½ hours.

The exterior has slagged badly to a depth of a quarter inch. The interior is vesicular and swollen, but not coarsely, and the fractures appear smooth and vitrified unless examined closely. Color is blue throughout. Not analyzed.



Figure 18. Showing cross-section of Draw trial No. 40, drawn at  $1130^{\circ}\text{C}$ , after 110 hours.

Color, blue or black throughout. Whole body very vesicular, swollen to a sponge, inside and outside. The swelling has about trebled the volume of the brick. This was the last brickette in Burn C.

## CARBON.

*Method of Analysis.* The powdered samples were first ground still finer to an impalpable powder in an agate mortar. One gram was taken for analysis. This was digested at a gentle heat in a mixture of 15 c. c. hydrofluoric and 5 c. c. sulphuric acids till practically everything except carbon was dissolved. The liquid and residue were then washed into a beaker containing 200 c. c. of cold boiled water in order to dilute the hydrofluoric acid, thus rendering it safe to work with and at the same time preventing it from attacking the asbestos filter used in the next step. The liquid was then filtered through purified asbestos, in a Gooch crucible. The filter and carbon were washed with cold boiled water and dried.

The asbestos and carbon together were then ignited in a combustion train. The train used was one of the ordinary kind with a twenty-burner furnace and a Jena glass tube, in which the sample is ignited in a slow stream of pure oxygen. The products of combustion are first passed over red hot copper oxide in order to convert any carbon monoxide ( $\text{CO}$ ) into carbon dioxide ( $\text{CO}_2$ ); secondly, over hot lead chromate which holds any sulphuric or sulphurous acid present forming lead sulphate, and which also retains a part of any hydrochloric acid which might be present, forming lead chloride; thirdly, over silver foil, which catches and holds any chlorine escaping the lead chromate, forming silver chloride; fourth and finally, over calcium chloride which takes out any moisture present.

The gases were then passed through a weighed set of Liebig's absorption tubes containing potassium hydroxide solution, sp. gr. 1.27, and a guard tube containing soda-lime. These absorb the carbon dioxide in the gases. The increase in weight of the bulbs and guard tube is considered to be carbon dioxide, and from this the weight of carbon is calculated.


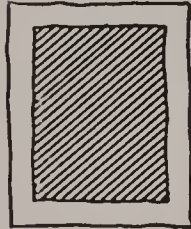
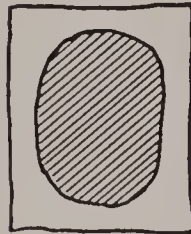


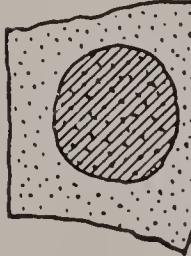

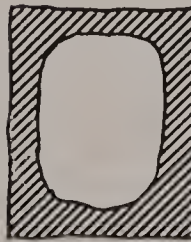
It was found that the carbon in the samples burned unusually slowly, and without appreciable glow, so they were kept at a bright red heat for forty-five minutes to insure complete combustion. The ordinary time allowed for a combustion of the graphitic carbon in pig irons or steels is only fifteen minutes.

*Results.* No question exists in the mind of anyone as to the absence of carbon from the red, so-called oxidized portions of



bricks. It is only suspected of being present in the black discolored portions, or cores, where it is thought by some to be the direct cause of the dark coloration. Accordingly, only a few of the samples were examined for carbon, and in those, *only the dark interior core*, not the red exterior. In one case only, Draw No. 37, was the exterior tested for carbon, and this was where a previously red brick was heavily and continuously reduced and blackened on the surface for a half inch or more, and in which the presence of some *deposited* carbon would have been not unnatural. None was found, however.

FIG. 19. SHOWING RESULTS OF CARBON ANALYSIS.

Appearance of Sample	Description of Trial Piece from which Analysis was made	Carbon Determinations	Average per cent. Carbon
	Raw Clay.	2.876 ..... 2.872	2.874
	Draw No. 1. Thin Exterior Shell of Pale Red. Core large and very black Drawn at 710 degrees, 17½ hours from beginning burn. Very soft.	2.310 ..... 2.310	2.310
	Draw No. 4. Exterior shell thicker and little stronger red. Core large, but paler color than 1 Drawn at 805 degrees C., 31½ hours from beginning of burn. Very soft.	1.160 1.170 1.190	1.173
	Draw No. 7 Exterior shell much thicker. Fair red. Core small and very pale color. Drawn at 980 degrees C. in 44 hours from beginning of burn Not vitrified.	0.150 ..... 0.152	0.151
	Draw No. 8. Exterior shell vitrified red. Core, vitrified, dark blue color, and more glassy than red portion. Drawn at 1080 degrees C in 47½ hours from beginning of burn.	0	0
	Draw No. 9. Exterior a little spongy from over-fire, red. Core considerably swollen and black. Drawn at 1100 degrees C in 48½ hours from beginning of burn.	0	0
	Draw No. 14. Spongy black core from which the red shell has been cracked loose. Enormously swollen. Drawn at 1210 degrees C. in 53½ hours from beginning of burn.	0	0
	Draw No. 37 Exterior black from heavy reduction. Interior still red. Both are dense and break in glossy fractures. Exterior was analyzed. Drawn at 1030 C. in 106½ hrs.	0	0

*Rate of Loss of Carbon.* The raw clay contained a very high amount of carbon to attempt to work. Shales of the same formation often contain 5 or even 10% of carbon, but are then considered practically unworkable.

Sample No. 1, drawn at  $710^{\circ}\text{C}$ , showed a black friable core, containing 80% of the initial carbon. Sample No. 4, drawn at  $803^{\circ}\text{C}$ , showed a little harder core, a little less glossy black, and having a carbon content of only 40.7% of the initial amount in the raw sample. Sample No. 7, drawn at  $980^{\circ}\text{C}$ , shows a grayish black core, one inch in diameter, and having only 5.2% of the initial amount, or in actual percents, 0.15 of 1% of the weight of the brick. Just where the last of the carbon goes out is not known, but sample No. 8, drawn at  $1080^{\circ}\text{C}$ , showed a black vitreous interior in which there was no carbon found, and there was no sign of puffing or vesicular structure, in either red exterior or black core. The appearance of this brick is well shown in Figure 9.

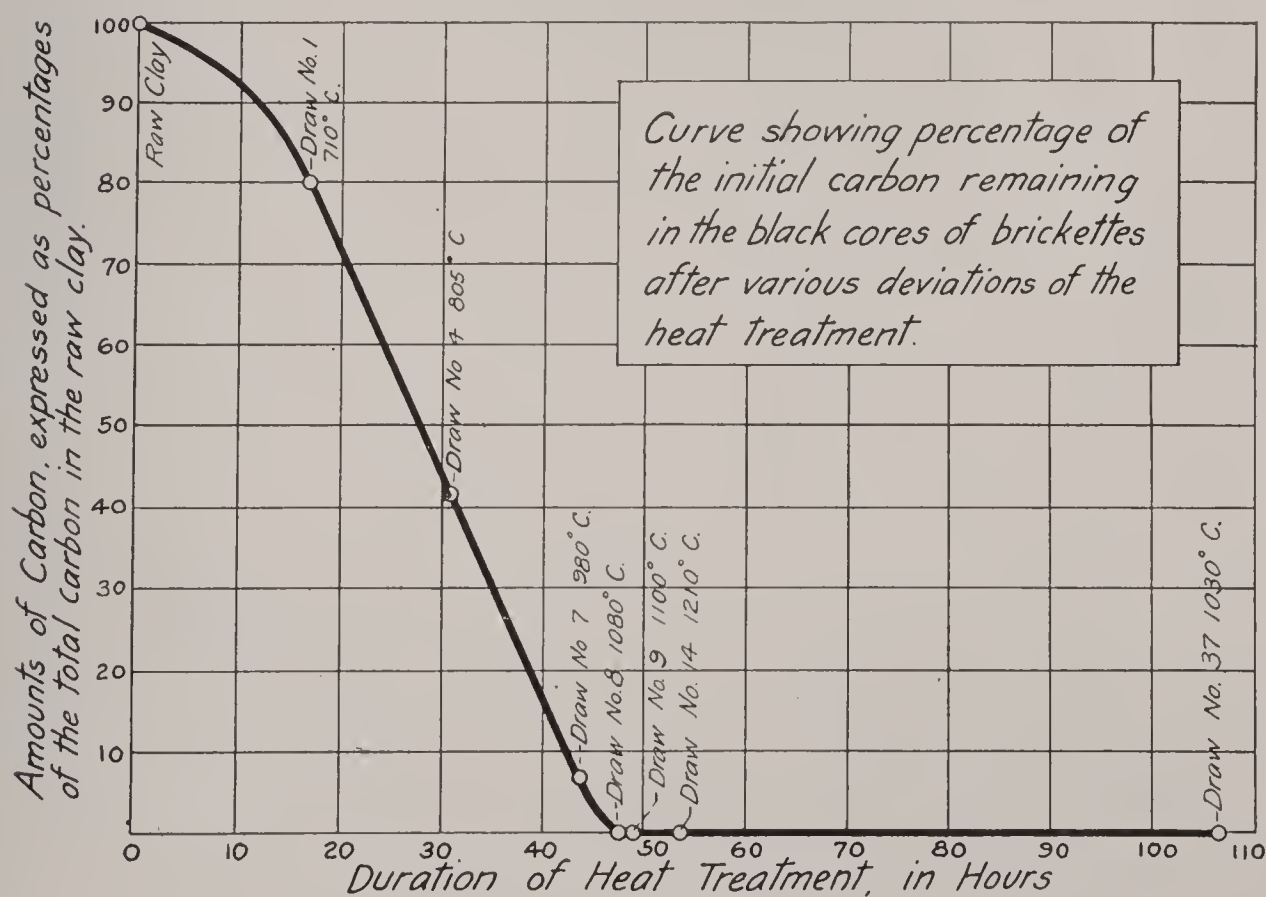


Fig. 20.



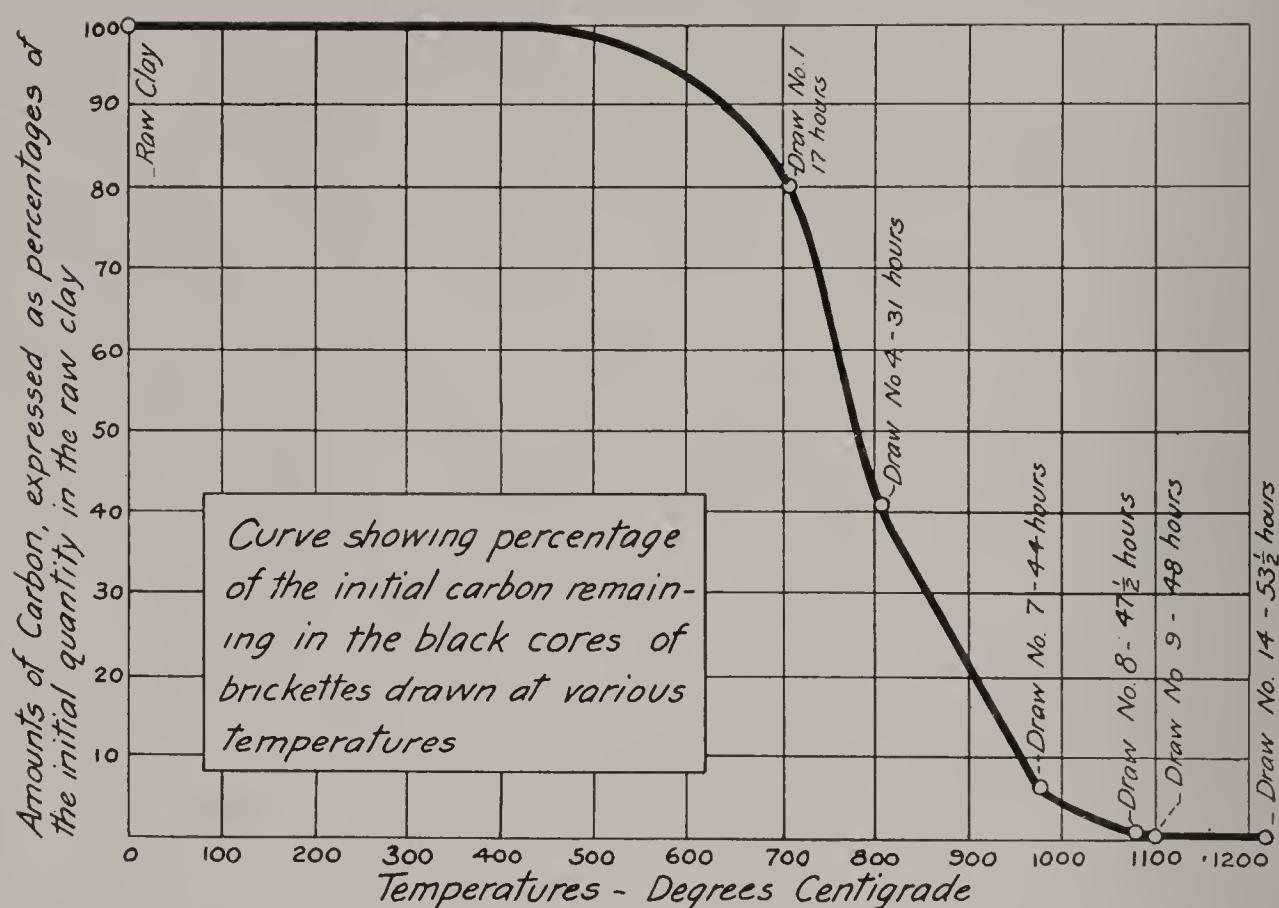


Fig. 21.

*Relation between size and density of black cores.* The rate of loss of carbon in this series of tests has brought attention to a point not properly appreciated before, at least by the writers, viz., that the size of the core is not a good gauge of the amount of the carbon it may be harboring. In this series of brickettes, the size of core changed but little from Draw No. 1 to Draw No. 5, but the amount of carbon was decreasing in these cores steadily, as was shown by the drop between Draw 1 and 4, 2.31% to 1.17%. Similarly, between No. 4 and No. 7, although the core shrank one half in size, the carbon fell away by about nine-tenths, or 1.17 to 0.151.

In this experiment, it was the design in Burn A to start the black coring reaction while plenty of carbon yet remained in the trials, and judging from the size of the cores we should have succeeded. This method misled us, however, so that when we reached vitrification, our carbon had wholly disappeared. It had, however, left a black core in its place, but one due to other causes, to be discussed later.

*Negative evidence on coloring by carbon.* The results reached, therefore, do not settle the point as to whether the black cores in vitrified bricks *may not* be due to actual carbon enclosed

in them. They show that no carbon existed in *these* bricks when they reached vitrification, although black cores of large extent remained, and later developed their characteristic effects. They confirm the analyses made by Prof. Lord for this committee, quoted on page 14, in that when the wares reached vitrification, no carbon remained. But the fact that the analyses show that the cores were already reduced to low carbon content (about 1%) before the heat was raised above 800°C, and the fact that the brickette contained only 0.151 carbon just before reaching vitrifying temperatures, does not enable us to say with authority that carbon *may not* be found as to the colorant in some vitrified clay wares.

Hopwood\* and Jackson found carbon in the black non-vitrified portions of abnormally fired clay wares. However, the samples examined by them were not, as far as we know, bloated, or near the bloating stage. We are willing to admit the probability of the truth of their statement that "the black internal colouration of abnormally fired clay wares is due principally to free carbon" when the statement is made in reference to very soft-burned wares, or to wares that have been scarcely oxidized at all, but do not think that it applies to hard-burned wares that have been tolerably well oxidized, such as No. 2, or the puffed samples up to No. 14.

*Theory as to the disappearance of the carbon from seemingly vitrified samples, without swelling.* In the report of last year,† the theory was tentatively put forth "that the carbon remaining in the clay at the beginning of vitrification was converted into carbon monoxide or dioxide by reduction of the ferric or ferrous oxide, and held in the clay under pressure, and which therefore would escape in grinding the sample preparatory to making an analysis, and thus would not show up in an analysis as free carbon. When the temperature was raised to a point at which the clay began to soften, the constantly increasing pressure of the gases would cause the softened mass to swell and develop a vesicular structure."

This theory has received further consideration, and the following analysis of the conditions of the case has been made:

Suppose all the carbon did not go out during oxidation and

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\*Trans. North Staffordshire Ceramic Society, 1902-1903, page 105.

†Influence of carbon in the burning of clayware, 2nd Report, Com. on Tech. Inves., N. B. M. A., 1904.

that 0.1 of 1% of the weight of the brick consisted of free carbon, and that this was converted into carbon monoxide. The brick weighs approximately 1500 grams. One-tenth of one per cent. of 1500 grams = 1.5 grams of carbon. Where carbon monoxide (CO) is formed, 12 parts of carbon unite with 16 parts of oxygen to form 28 parts of carbon monoxide. Then by proportion,

$$12 : 28 = 1.5 : X$$

$X = 3.5$  grams of carbon monoxide formed.

One liter of carbon monoxide at  $0^{\circ}\text{C} = 1.234$  gr. (Smithsonian Physical Tables).

By calculation, one liter of carbon monoxide at  $1000^{\circ}\text{C}$  and ordinary atmospheric pressure = 0.2643 gr.  $3.5 \div .2643 = 13.20$  liters of carbon monoxide at  $1000^{\circ}\text{C}$ , and one atmosphere (14.7 pounds) pressure. 1 liter equals 61 cu. inches.  $13.20 \times 61 = 805.2$  cubic inches.

Since the brickettes used in this investigation measured about  $3 \times 4 \times 4$  inches or 40 cubic inches, the gas evolved by the oxidation of 0.1% of carbon would have made a bulk, under normal atmospheric pressure, of  $805.2 \div 40$ , or 20 times the volume of the brickette. If 10% of the sample were free open pore space, the volume of gas would be 200 times as large as the space available.

As the volume of a gas varies directly with the temperature and inversely with the pressure, and if the volume were maintained constant, and the temperature were increased, the pressure would vary directly as the temperature, then it follows that in the case above cited the pressure in the cold brickette would be according to the proportion: As the volume of the pore spaces are to the free volume of the gas generated, so is free pressure of the atmosphere to the pressure generated; or, expressed in figures,

$$1 : 200 :: 14.7 : X$$

where  $X$  is equal to the pressure that would be necessary to compress the gas from 200 volumes down to one volume. On solving the proportion, this is found to be equal to 2940 lbs. per square inch.

If this theory were sound, the gas generated by the reduction of the iron would be held under this enormous pressure in a brickette which had been chilled down to the atmospheric temperature from the partially vitrified condition, without giving any sign of its presence, which does not appear reasonable. It seems, therefore, that this theory is not tenable, and that if either



carbonic oxide or acid is generated by reduction of iron or otherwise, that it must speedily escape through the pore system or else swell the clay and produce a vesicular structure. The absence of carbon by analysis must be construed as proof of its escape from the clay.

*Deposition of carbon by heavy reduction.* A test was made on the black exterior of No. 37 for carbon but none was found. Carbon may be deposited from fire gases into the pores of a porous clay ware, as familiarly seen in the German "Blue Smoked" roofing tile, but it is hard to see how it could get into the interior of a vitrified ware to any large extent.

*Summary.* The results of the work done on the carbon may be summarized as follows:

I. The carbon was responsible for the color of the dark cores of this clay during the early portion of the burn while the ware was still very soft and porous.

II. The carbon in this core burned away steadily during the oxidation and early vitrification period, leaving none in the clay after complete vitrification had occurred.

III. Ten other samples of black cored or reduced clay wares of various sorts showed no carbon present in the dark colored spots.

IV. In this clay, when the carbon had been recently expelled at the time when complete vitrification was reached, the brickettes formed black cores of shape and extent similar to that recently vacated by the carbon.

V. The active or immediate cause of these black cores must be sought outside of the carbon, which seems to be generally absent when the core is formed.

VI. The carbon in a vitrified body could not be converted into gas by oxidation without causing vesicular structure to develop. But dark colored vitrified cores do develop constantly, without showing any signs of vesicular structures for long periods after formation. This seems to still further militate against the presence of carbon being a direct cause of the black coloration.

VII. That in the case of dark coloration produced by heavy reductions in carbonaceous atmosphere in a body previously well oxidized, no carbon was found in the dark areas, and the cause of the color must be sought elsewhere.

VIII. That authentic cases of the deposition of carbon in

the interior of clay wares, by long continued heating in heavily reducing atmospheres, can doubtless be shown, but that in such cases, the clay wares are porous, and the reduction is heavier than is likely to be produced in ordinary kiln firing, and the deposition of carbon is obtained by special treatment, designed for the purpose.

## IRON.

The status of this element being in serious question, a considerable number of determinations were run, on total iron, and ferrous oxide, the ferric oxide being obtained by difference.

*Method of Analysis. Total Iron.* A one gram sample was fused with ten times its weight of dry sodium carbonate. The fusion was digested until completely disintegrated in warm water, was then acidulated with hydrochloric acid and evaporated to dryness. The residue was moistened with hydrochloric acid and the soluble portion was dissolved in warm water, and the silica was filtered off and thoroughly washed. Sulphuretted hydrogen gas was then passed into the filtrate to precipitate any platinum that might have been dissolved from the crucible during the fusion. The solution was filtered, boiled to drive off the excess of sulphuretted hydrogen, filtered again to remove free sulphur, and then made alkaline with ammonium hydroxide, and boiled. The precipitate, consisting of hydroxides of iron and aluminum, was allowed to settle, the supernatant liquid was decanted off, and the precipitate was washed onto a filter. The precipitate was dissolved again in hot dilute hydrochloric acid and collected in a clean beaker. The solution was diluted to 100 c. c., and heated to boiling. The iron was reduced by stannous chloride, added drop by drop. The excess of stannous chloride was then neutralized by adding an excess of mercuric chloride. Then the iron was determined by titrating with a standard solution of potassium bi-chromate.

This method is considerably longer than the ordinary iron determination. All of the steps between the separation of the silica and the reduction by stannous chloride are generally omitted. In fact, some chemists do not even separate the silica. We tried to use the solution obtained immediately after the separation of the silica, but found that our results were high. In order to get our hard burnt vitrified clays into solution it was necessary to use ten grams of sodium carbonate, and to heat it to



the highest limit of the blast lamp for ten or fifteen minutes. The strong alkaline fusion always attacked the crucible, appreciable amounts of platinum being separated by the proper treatment.

*Ferrous Oxide.* A one gram sample was digested at a gentle heat in a mixture of 15 c. c. hydrofluoric acid, and 5 c. c. sulphuric acid in an atmosphere of carbon dioxide. This was effected in the following manner: The sample was placed in a platinum crucible and moistened with a little freshly boiled water, which had been cooled down to the atmospheric temperature again. The crucible was placed in a support on the center of the bottom of an enameled iron pan, and the pan was placed on a tripod. A bell jar, improvised from a two liter bottle with its bottom cut out, was set down in the pan, over the crucible. The space between the bottle and the sides of the pan was filled in with fine white sand. The sand made a layer  $1\frac{1}{2}$  inches wide and 2 inches deep, and formed a fairly tight seal. The bottle was fitted with a two-hole rubber stopper. In one hole was placed a small separatory funnel with its stem leading down into the top of the platinum crucible. In the other hole was placed a small piece of glass tubing to act as an exit tube. The carbon dioxide was led in from a Kipp generator through the sand layer and under the edge of the bell jar by means of a piece of bent glass tubing, and the gas was discharged below the level of the top of the crucible. Being heavier than air, it filled the bottom of the space first, then gradually rose in the bottle until finally it overflowed at the top through the exit tube. At the beginning of a determination, the gas was passed into the jar at a rather rapid rate till all the air was displaced and the gas coming from the exit tube would promptly extinguish the glow of a match. Then the mixture of hydrofluoric acid and sulphuric acid was allowed to run down through the funnel into the crucible. The flow of carbon dioxide was allowed to slacken to a small but steady stream, and a small flame was placed under the pan. The flame was so regulated that fumes of hydrofluoric acid were given off, but the sulphuric acid was not brought to its boiling point. When practically all of the sample had gone into solution, the glass cover was raised above the level of the crucible, without removing the flame or stopping the flow of carbon dioxide, the crucible was siezed with a pair of platinum tipped crucible tongs and quickly



dropped into a beaker of cold boiled water. This solution was then immediately titrated with potassium bichromate solution. As there had been no chance for either oxidation or reduction of the iron, during solution, then the iron which reacted with the indicator represented ferrous oxide in the sample.

The solution of the harder burned samples in hydrofluoric and sulphuric acids was a difficult thing to accomplish without danger of oxidizing some of the ferrous oxide to ferric oxide by means of the hot sulphuric acid. An ordinary rock analysis is considered rather difficult, when it is possible to disintegrate the sample with a mixture of acids heated to the boiling point of water. In our work, on account of the resisting power of hard burned vitrified clay powder, it was impossible to disintegrate the samples unless the acids were heated till the hydrofluoric acid had largely distilled off at  $110^{\circ}$ — $120^{\circ}\text{C}$ , but of course it was necessary to keep the temperature well below the boiling point of the sulphuric acid.

*Ferric Oxide.* The total iron and the ferrous oxide being known, it was easy to obtain the amount of iron existing as ferric oxide by difference; it would be rather difficult to make a direct determination of it; and none was attempted.

*The Results.* The figures obtained by the above methods from the samples before described are given in the following table:

TABLE NO. 4. RESULTS OF IRON ANALYSES.

Designation of Burn.	Number of Draw-Trial	RED PORTION OF BRICKETTES			BLACK PORTION OF BRICKETTES.		
		Amount of Iron existing as Ferric Oxide expressed in terms of the metal.	Amount of Iron existing as Ferrous Oxide expressed in terms of the metal.	Total amount of Iron found expressed in terms of the metal	Amount of Iron existing as Ferric Oxide expressed in terms of the metal.	Amount of Iron existing as Ferrous Oxide expressed in terms of the metal.	Total amount of Iron found expressed in terms of the metal.
Raw Clay	1	1.84 1.79	3.58 3.58	5.42 5.37	) Calculated on basis of the burnt clay viz., allowing for a loss of 11.16% of the clay in firing.		
Burn A	1	5.02 4.97	0.31 0.31	5.33 5.28	0.67 0.70	4.56 4.61	5.23 5.31
	4	5.49 5.45	0.36 0.33	5.85 5.79	0.62 0.67	5.23 5.18	5.90 5.85
	7	5.34 5.28	0.56 0.56	5.89 5.85	0.52 0.52	5.33 5.33	5.85 5.85
	9	5.31 5.23	0.95 1.02	6.25 6.25	0.36 0.36	5.90 5.90	6.25 6.25
	14	No red in	color this	produced sample	.... ....	6.15 6.15	6.15 6.15
Burn B	21	5.43 5.45	0.51 0.51	5.95 5.97	These bricks had no black core or black exterior.		
	22	5.46 5.54	0.61 0.61	6.08 6.15			
	25	5.54 5.53	0.61 0.64	6.15 6.18			
	28	5.54 5.54	0.61 0.61	6.15 6.15			
	29	5.54 5.51	0.71 0.74	6.25 6.25			
Burn C	37	6.55 6.50	0.11 0.11	6.67 6.61	0.35 0.30	6.26 6.26	6.61 6.56

*Analysis of the Results. The totals.* The total amount of iron found in the different brickettes, and in the different parts of the same brickettes, is on the whole quite uniform, but there are some interesting discrepancies. In no case in the 90 determinations is there any serious divergence between the total irons found in the red portion and the black portion *of the same brick*. The greatest is about 1.6% of the average amount of iron present. In most cases, the checks are very good. In some instances there were determinations made which departed widely from the general run, and these were remade until the trouble was cleared up and the determinations became consistent and duplicatable.

When we consider the checks between different brickettes, the agreement is not so good. The clay from which the brickettes were prepared should produce a more homogeneous distribution of the iron than was found in this study. There seems no reason on the face of this case, why individual bricks should have varied more than 2 or 3% of the average contents of the batch. We find as follows:

TABLE No 5

No.		Average of Iron Determinations
BURN A.		
0	Raw clay .....	5.40
1	Softest, but little oxidized .....	5.29
4	Soft, partially oxidized .....	5.84
7	Much harder, small core .....	5.86
9	Vitrified, beginning to swell .....	6.25
14	Swollen to a sponge .....	6.15
BURN B.		
21	Oxidized, granular, soft .....	5.96
22	Oxidized, granular, harder .....	6.12
25	Oxidized, vitrified .....	6.16
28	Oxidized, vesicular .....	6.15
29	Oxidized, very spongy .....	6.25
BURN C.		
37	Vitrified, not yet vesicular .....	6.61



There is a curious increase to be noted here between the raw clay and the burnt, and between the soft burnt and the hard burnt of each series, for which no adequate explanation can now be advanced. The natural explanation of the loss of volatile constituents has been forestalled by the calculation of the iron found in the raw sample into what it would be on the burnt sample, allowing 11.06% loss in heating.

There are also discrepancies to be expected in the percentage of iron found in different trials because of its distribution in different forms in them, but these are small. The lower amount of iron in Sample 1 than the calculated figure of the raw clay is due to there still being the bulk of the carbon left in Sample 1, while the other figure is assumed on the basis that the carbon has been sent out. But the very marked increase in iron in all the succeeding samples cannot be explained on any such basis.

Between samples 4 and 29, the fluctuations from the average are not beyond what might be termed ordinary working margins in analytical work. But No. 37 and No. 1 vary 1.32% or 21% of the above average figure.

The natural explanation to give is that of extensive alteration by volatilization of the clay ingredients. This is suggested in samples 14 and 29, which are the two most vesicular samples of their respective burns that were tested, but this theory is untenable in view of the iron content found in No. 37, which was not yet vesicular.

There is, of course, the hypothesis that the work was incorrect, and badly done. But as it was performed at leisure, by one man only, who spent all needed time on it and never left a sample until duplicate tests checked nicely, it is difficult to accept this idea as correct, (especially as in most of the cases, duplicates made from separate samples of different parts of the same brick showed on assembling, substantially the same amount of iron present). It seems, therefore, an interesting question to carry through at a subsequent investigation.

*The Ferrous Determinations.* The ferrous iron determinations were very nice and regular, so far as ability to check determination is concerned. These determinations did not give much evidence on the problem brought up by the totals, except in the case of No. 14 and 37, in which the ferrous iron alone closely checked the high totals of the same samples.

*The Raw Clay.* In the raw clay, 66% of the iron was in the ferrous condition. The mineral in which it occurs is probably ferrous carbonate, but there is also a considerable amount of pyrite and probably a little ferrous sulphate.

*The Distribution of the Iron in the Red Portion of the Brickettes.* The iron seems to have changed over into the ferric form with comparative ease and completeness, as the carbon was burnt out and the clay took on its red color. In fact, the oxidation attained immediately after the removal of the carbon at temperature of 700°C and 800°C was more complete than that observed as the temperature rose. Thus the percentages of ferrous oxide remaining in the red portions of the various brickettes was :

TABLE No. 6.

No.		Per cents. of the Total Iron Present
	BURN A.	
0	Raw .....	33.00
1	At beginning of oxidation period.....	5.81— 5.87
4	Oxidation period well advanced.....	6.15— 5.70
7	Vitrification period begun. Small black core .....	9.59— 9.57
9	Vitrified and vesicular .....	15.20—16.30
	BURN B.	
21	Core completely gone, bright red through out .....	8.57— 8.54
22	Harder but not vitrified .....	10.03-- 9.91
25	Vitrified but not vesicular. Red.....	9.91—10.35
28	Vesicular, just beginning to swell strongly	9.91 9.91
29	Vesicular, spongy mass .....	11.36—11.84
	BURN C.	
37	Vitrified red center. Exterior black and reduced .....	1.64— 1.64

The above facts are shown graphically in the following curve sheet, Figure 22.

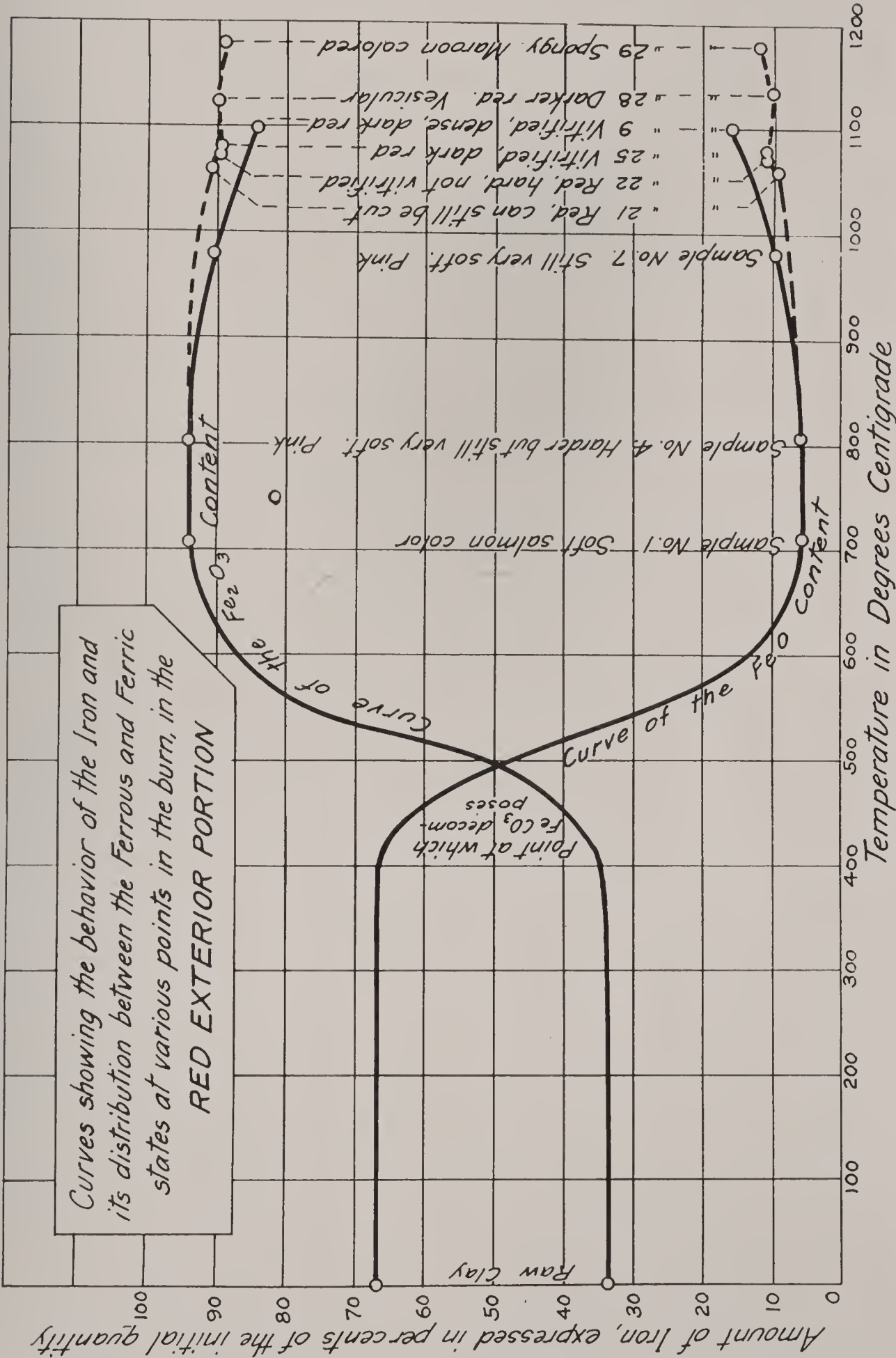


Figure 22.



A study of the above table and curves shows:

1st. That the iron does not seem to go wholly into the ferric form, even after prolonged periods of firing in oxidizing atmospheres. It behaves in a manner analagous to carbonate of calcium, when heated, which loses  $\text{CO}_2$  until but a small quantity remains which cannot be expelled without undue heat and conditions not commercially attainable. Many other illustrations of the same principle of chemical equilibrium are observed in chemical decompositions. Red clay wares, no matter how bright in color, are thus likely to contain some ferrous oxide.

2nd. That increase of temperature above that favorable to oxidation ( $800^\circ\text{C}$ ) and running into the vitrification zone, seems to actually militate against the oxidation. A counter influence of some sort is set up, by which the proportion of ferrous oxide increases 50% over its minimum, or from 6% up to 9 or 10%. Here it seems to tend to remain, as samples of very varied physical structure and degree of hardness clearly show. Numbers 7, 21, 22, 25 and 28 illustrate this condition.

3rd. That driving the temperature up to the point where the clay becomes markedly scoriaceous or vesicular seems to tend to still further increase the ferrous iron. This tendency is not clearly proven, for in No. 29, which was very scoriaceous, though a good red color, the increase in ferrous oxide was small, while in No. 9, which contained a large black core, the red portion jumped up to 15 or 16% of ferrous oxide. It may have been influenced to do this by the passage of gases from the interior on their way out. Carbonic oxide ( $\text{CO}$ ) or sulphurous acid ( $\text{SO}_2$ ) might readily exert such an effect.

4th. The fact that clays may fuse and become scoriaceous without thereby blackening or undergoing a breaking down of  $\text{Fe}_2\text{O}_3$  to  $2\text{FeO}$  as a necessary corrolary is clearly shown by these samples. This point is commonly illustrated in many other clays, but as the idea has been advanced by one of the present writers (Orton) that fusion means accompanying or preceding blackening, it is perhaps worth while to call attention to the untenability of this hypothesis.

*The Black Portion of the Brickettes.* The reducing agent which causes the black coring reaction, whatever it is, is more powerful in its operation than the oxidizing reaction which operated in the red colored areas, for the percentage of ferric

oxide in the black areas became constantly less with increasing temperatures until none remained. It would seem that the presence of either carbon or sulphuric matter intimately mixed with the clay mass is powerfully efficient as a dioxidizer of iron. It also appears that even when it is shown by analysis that no carbon remains, reduction of ferric iron to ferrous still takes place.

Thus in draw trial 7, the amount of carbon found by test was 0.15% and the ferric iron in the black core was 0.52%. In No. 9, the carbon was 0, while the ferrous iron had fallen to 0.36. In sample 14, however, there was no carbon, but the ferric iron had now fallen to zero. The loss of 0.36% of ferric iron from the black core must therefore be accounted for without considering carbon as a possible cause. The possible influence of sulphur as the cause of this reaction will be considered elsewhere.

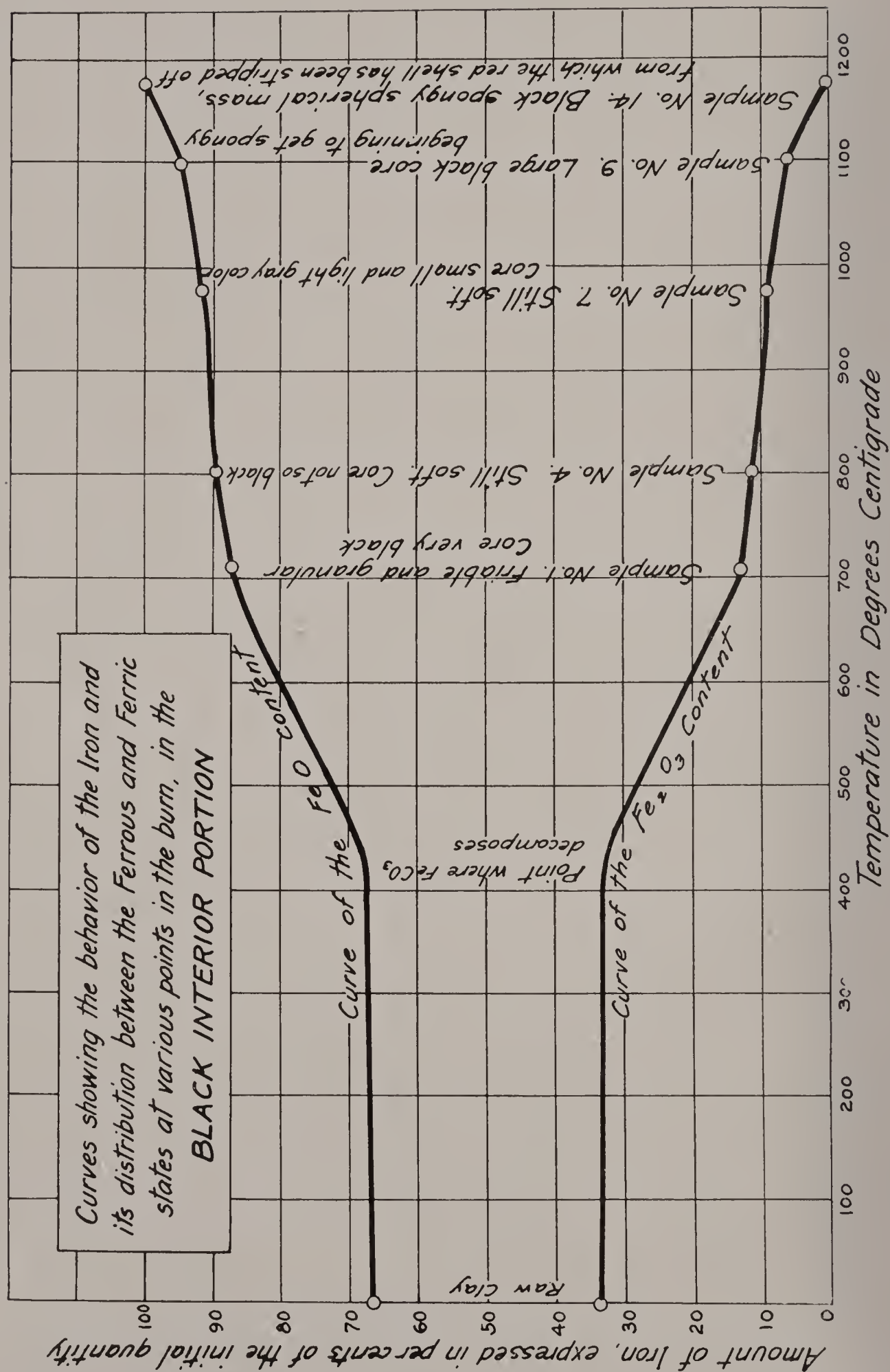


Figure 23.



This reduction could not have proceeded from outside inwards, because in every case there was a shell of red matter encompassing the black portion. In Burn C, one test brickette only was examined. We find it significant in two respects. 1st, its red portion is the nearest to completely oxidized of any sample in the whole test, there being one about 1.6% yet in the ferrous condition.

It had been under oxidizing influences for nearly a hundred hours. In the reduced exterior, on the other hand, 95% of the iron was in the reduced condition. As all visible signs of reducing agents had been burned out long since, and there was no deposition of carbon in the pores of the clay, this intense reduction was no doubt due to the influence of the gases of the kiln atmosphere. As the pores of the clay were all or nearly all closed at the time, the action must have been an intermolecular one, the gases continuously taking the oxygen from the molecules on the surface, and these molecules taking the oxygen from the molecules next to them toward the interior, and so on till oxygen was finally being transferred from deep in the interior of the brick to the surface.

*The Role Played by Iron.* The role played by iron in the vitrification of clay wares is understood to but a limited extent as yet. We know in a general way that iron oxide reduces the temperature at which clays are burnt, i. e., that red burning clays, high in iron, are burnt at temperatures considerably below the buff burning clays low in iron, and still further below the white burning clays in which iron is practically absent. We know that it serves a useful purpose in this respect, and that the bodies produced by vitrification of ferruginous mineral mixtures are often just as desirable in every way for the practical uses of life as the lighter colored ones, which require more fuel and are therefore more costly. But we have as yet little detailed and quantitative knowledge of the exact effect of iron in the various mineral mixtures which we call clays.

There has been much speculative discussion about the effects of iron in clays. Much of it centers around the three following topics:

I. The Black-Coring reaction. As an improperly oxidized clay "black-cores," i. e., shows fusion and vesicular structure in

the unoxidized area, is this premature fusion due to the state of oxidation of the iron?

II. The Blue-Stoning reaction. As a properly oxidized clay gradually darkens in color when subjected to increasing temperatures during normal burning, is it due to changes in the state of oxidation of the iron?

III. The final Slagging or Over-fire reaction. As a properly oxidized clay slags and becomes spongy from over-fire under oxidizing conditions, is it due to changes in the state of the oxidation of the iron?

These topics will be taken up in order, and studied from the point of view of the data now on hand.

*The Black-Coring Reaction.* It has been stated by Wheeler that ferrous oxide becomes active in slagging the clay about  $200^{\circ}\text{C}$  below the temperature at which ferric oxide would become an active flux.

On the basis of this statement, an explanation of the black coring reaction has been built up by Orton and others, to the effect that this early or premature fusion in the unoxidized area of the clay, occurring while the clay is still disengaging gases from its interior parts, is the cause of the black swelling and scoriaceous slag spots in the center.

It was observed in this study, that the swelling of the brickettes from the black-coring reaction, and that which came from the simple overheating of the well-oxidized clay, both occurred in a very narrow temperature range—between  $1080^{\circ}$  and  $1100^{\circ}\text{C}$ . In both burns A and B, the swelling occurred while the kiln was being fired with a nice oxidizing atmosphere. In Burn C, which was fired under heavy reducing conditions, the first test piece to show clearly vesicular structure from over-heating was No. 38, which was drawn at  $1060^{\circ}\text{C}$ , but which had been fired rapidly up to  $1100^{\circ}\text{C}$  shortly before. When the remaining brickettes were again heated up from  $1060^{\circ}$  to  $1100^{\circ}$ , they promptly swelled and much more markedly than No. 38.

It is safe to say, then, that in all three burns, puffing occurred between  $1080^{\circ}$  and  $1100^{\circ}\text{C}$ . In all three cases, the puffing occurred at the same stage in the vitrification process, a short time after the vitrification had reached the point of best development. In each burn, a sample with dense, solid glassy structure and almost no porosity was secured before samples showing signs



of vesicular structure began to appear. In samples having a red or oxidized portion and a black or reduced portion, the black portion *became vesicular a short time before the red portion*. The black portions become more vesicular than the red also. In No. 9, the black core is noticeably vesicular while the red portion is minutely vesicular in some parts. In No. 37, the black part is minutely vesicular while the red portion is still sound, but the next sample drawn a short time afterward is vesicular in both the black and red portions.

We can say then that in this clay, the breaking down and development of vesicular structure occurred at a distinct but very slightly lower temperature in those portions in which the ferrous oxide was high and ferric oxide low than in those portions where the bulk of the iron present was in the ferric condition.

Also, that in all cases, a dense, solid, apparently strong body of a blue color was obtained where the iron was predominately ferrous, exactly comparable with the dense solid strong body of a red color, where the iron was mainly ferric, and that these stages were produced and passed through before either portion became vesicular.

On the other hand, instances are numerous and undeniable where red burning and buff burning clays do develop a vesicular core which swells and deforms the ware, while the encompassing normal portion of the ware is not in the least degree vesicular nor near its point of failure by over-fire. Observations of the product of commercial plants often discloses wares in which the exterior oxidized and normal portion of the ware in different parts of the kiln has been subjected to wide fluctuations of temperature, during which it has passed from a low grade of vitrification up to a high grade of complete vitrification—evidently covering considerable time and temperature interval—without showing any signs of over-firing, while the interior core has meanwhile undergone profound changes of density and degree of fluidity. This evidence is too well established and confirmed by too much industrial practice to be easily overthrown.

We have, then, two dissimilar cases, 1st, the clay of the present study, which black-cores and swells at a low temperature, and at a very slight temperature interval before the red properly treated portion also swells and fuses. And 2nd, the general run of red- and buff-burning clays, such as are used for paving brick



and sewer pipe, which black-core and swell a long, but not yet accurately measured interval, before the red portion begins to break down from over-fire.

It should be said that there are undoubtedly many clays that do belong in the former class; many have been observed to give identical results in test-kiln firing, but we happen to possess no measured data concerning them.

The question now arises—how can ferrous iron be responsible for early fusion in one case and not in another? Before answering this, another question should be asked, viz., are we really sure that ferrous iron is the cause of the early fusion? In other words, is the fundamental statement of Wheeler as to the difference in melting point of the ferrous silicate true or not? There seems some reasons for doubting it. For instance, in America, many paving blocks are made with a blue or reduced exterior zone, sometimes half an inch or an inch in thickness, covering a red core of vitrified material. Such bricks are made by heavy reduction after the burn has been properly carried through the vitrification process. This condition was produced in our Burn C, in sample No. 37, and those following it. The chemical test of No. 37 shows that the iron was thoroughly reduced by the gaseous treatment, and that practically no ferric iron remains in the blue zone, and there seems reason to expect a similar state of things in other clays showing the same color changes in response to the same treatment. Now these blue-coated pavers often give most excellent results for strength and toughness in the rattler and in street use. On examining them carefully, the blue portion is not necessarily found to be vesicular or defective in structure by reason of its color change, nor is there any evidence of greater fusibility than in the red or ferric portion.

In England, blue-fired clay wares, like the famous vitrified brick of Staffordshire, the “Staffordshire Blues,” are made by thoroughly oxidizing the ware and vitrifying it in the normal manner, and then reducing the iron at a high temperature (1300°C). This ware is noted for its strength and durability.

This evidence seems to indicate that the mere existence of iron in the ferrous condition in a silicate, or the change from the ferric to the ferrous, is not necessarily accompanied with more easy fusion, or any signs of poor structure due to over-fire.

Looking at the other side of the problem, why do the black cores formed in clay wares so generally show the scoriaceous structure, and swell long before the red portions, unless from greater fusibility? The explanation suggested at this point is that the difference of temperature of fusion, if any exists, is not the controlling or predominating influence, and that the real factor is the relative volumes of gas which the two areas contain. It will be shown later in this report, that gases or gasforming impurities still occur in the black portions to a very much greater degree than in the red or oxidized portions. Supposing an equal and fairly complete degree of vitrification obtains in both the black area and the red, but that the former is disengaging gases rapidly and the latter is not. The red exterior will not swell, while the black interior will sponge up. The *apparent* vitrification of the two areas will be far apart, without any necessary difference existing in this respect.

*The Blue-Stoning Reaction.* By this term is meant the change from lighter to darker colors of red or buff shown by clays in passing through their vitrification range into over-fire. In some clays the changes are very gradual, and while great in total amount are never great between any two contiguous temperature periods. In others, the clay remains in nearly one tint for a considerable period of heat treatment, only to change suddenly from red to brown or black, or from buff to blue or gray. The intimate causes of this change are not known with any certainty, but there are two theories:

Seeger holds\* that:

1. This deepening in tint of red burning clay wares with increase of temperature is due to increase in density of ferric oxide

2. The increase in density of the ferric oxide is augmented by an increase in density of the ware itself, and especially by the closing of the pores upon vitrification.

3. The color will be influenced by the chemical condition of the ferric oxide; i. e., whether it is mixed with the clay mechanically, or is in combination with some of the constituents. Glasses and slags with a high content of ferric oxide have a brown color, and show tints such as free oxide never assumes.

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\*Collected Writings, p. 107.



It has been held by others\* that the marked deepening of color after vitrification was due to the breaking down of ferric compounds and the formation of ferrous silicate.

Considering the data at our disposition in this test, we find that in the exteriors of Burn A and in Burn B, both burns having been completed under oxidizing conditions, that there was a gradual darkening of color as the temperature rose. Starting from light salmon the color passed through pink and light red as vitrification temperatures were approached. When vitrification took place there was a perceptible deepening of red color, and as the temperature was carried still higher this color deepened into a dark red with a touch of brown in it.

These changes of color were accompanied by some chemical changes as well. The proportion of ferrous iron stood as shown in table 4, on page 63. A gradual increase in amount of ferrous oxide, with a gradual and proportionate decrease of ferric oxide undeniably took place, and would tend, on the surface, to support the second view given.

On the other hand, the changes in color were not coincident or coordinate with the changes in the status of the iron. No. 9, with 15-16 percent of its iron in the ferrous state, was much lighter in color than Nos 28 and 29, containing 9.91 and 11.84 percent of their iron respectively in the ferrous state. No. 28, with 9.91% of its iron in the ferrous state was much darker than No. 25 with 10.35%.

From the preceding experiments, we may say that the second theory is thus doubtfully supported by the evidence. The darkening in color seems to a great extent independent of the formation of ferrous oxide in the samples, and thus the theory of Seger is proportionately strengthened. The most that can be said for the ferrous oxide theory is that it might be a contributory cause without violence to the data found, but that it is not proven to have any vital connection with the phenomenon.

*The Over-Fire reaction.* The theory has been advanced that the puffing of properly oxidized clay ware on over-heating is caused by the breaking down of ferric oxide to form a ferrous silicate, with evolution of oxygen, the oxygen being supposed to cause the puffing.†

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\*Orton, Trans. A. C. S., Vol. V, page 424.

†Jackson, T. E. C. S., 1903-1904, page 43.



Sege<sup>†</sup> says, "I have often had opportunity to melt colorless glasses together with iron oxide without any other coloring agent. When the glass was clear, free from sulphuric acid, which is usually not the case, and the ferric oxide was purified from sulphuric acid, it was found that the oxide dissolved without any evolution of gas, and in oxidizing conditions produced a yellow to red brown color. I can therefore not yield the point that ferric oxide dissolves in the glass to form ferric-ferrous oxide with an evolution of oxygen."

The fusible matrix of a vitrifying brick is fairly comparable to a porcelain glaze batch. In both cases, we have a fusion of silica and approximately the same bases. If ferric oxide acts in a certain way upon going into solution in a glaze batch, why should it not act in the same way on going into solution in the matrix of a brick? Some easily fusible red burning clays are widely used as glazes under the name of "slips."

When our thoroughly oxidized samples went into vitrification and swelled as in No. 25 to No. 30, there was no notable decrease in the amount of ferric oxide. The small increase in the amount of ferrous oxide might easily have been due to the reducing conditions incident to raising the heat rapidly, or to the action of gases coming out from the core and affecting the iron as they passed through. The samples went into viscous fusion and yet the bulk of the iron stayed in the ferric condition.

Geo. C. Matson\* burned four different clays, and also a mixture of magnetite and feldspar to viscosity. He found that in every case the amount of ferrous iron in the viscous mass was much smaller than it was in the raw clay. It was also smaller than it was in the same clay burned only to a porous condition and not vitrified.

Hopwood\*\* notes that Sidot has shown that ferric oxide is changed to magnetic oxide by prolonged ignition at white heat, but goes on to say that "we can not infer from this that the ferric oxide in clays suffers such a decomposition when heated in clay ware kilns." He further states that he found no magnetic—that is, ferroso-ferric—oxide in tiles heated under oxidiz-

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<sup>†</sup>Collected Writings of Seger, page 1037.

\*Clay-Worker, XLII, No. 2, page 44. Also reproduced on page 19, this report.

\*\*Trans. Eng. Cer. Soc., 1903-1904, page 40.

ing conditions in a china biscuit oven, at a temperature of 1350°C. Hopwood and Jackson† fired ferruginous clay wares in an oxidizing atmosphere at a temperature of 1700°C without noticing any bloating.

Seger ascribes the yellow color of porcelain to ferric oxide and says‡ that during oxidation, porcelain will always be yellow. German porcelain is fired at a far higher temperature than red brick clays.

If the vesicular structure of clay ware was due to the simple overheating of ferric oxide, then this phenomenon ought to show itself at approximately the same temperature in all cases, but we find that clays break down and become spongy anywhere from 1100°C to about 1700°C.

In the tests made in this investigation, Burn A gives but little evidence. The ferrous oxide constituted 5.81, 6.15 and 9.50 percent of the total iron in Nos. 1, 4 and 7 respectively. During these changes the samples had changed from granular to vitrified red bodies but without swelling. In the next sample, No. 9, the ferrous oxide jumps up suddenly from 9.50 to 15.2-16.3, and at the same time the oxidized exterior of the ware swells and darkens in color.

In Burn B, the results are more valuable, because the samples cover the period more fully. The figures run :

TABLE No. 7.

No	Texture	Percentage of Iron in Ferrous condition
21	Vesicular spongy mass .....	8.57— 8.54
22	Vitrified and beginning to swell.....	10.03— 9.91
25	Vitrified and dense .....	9.91—10.35
28	Granular and harder .....	9.91— 9.91
29	Granular and porous .....	11.36—11.84

The proportion of ferrous oxide increases as the brickettes become harder, but changes in hardness are not accompanied by commensurate changes in status of the iron, as in numbers 25 and

†Trans. Eng. Cer. Soc., 1901-1902, page 110.

‡Collected Writings, page 1038.

28, for instance. Number 28 and 29 show a change in the right direction, but it is by no means proven that the cause of the increase in FeO was by breaking down of  $\text{Fe}_2\text{O}_3$ .

Burn C has no evidence on the point at issue.

The writers have had experience with a common brick clay, probably of alluvial origin, which passed from vitrification into fusion without undergoing the usual vesicular stage. It reached a sufficient degree of fluidity to flow down between two other bricks, where it chilled in a compact glassy mass, of brilliant black luster. This clay must undoubtedly have contained iron—probably a good deal of it—and presumably this iron had passed from the ferric to the ferrous state in part at least during the burning process, as the black color of the glass surely points to ferrous oxide. However, the mass did not suggest the slightest sign of vesicular structure, as it should have done according to the dissociation theory.

The figures obtained in this investigation do not go any great distance towards establishing the dissociation theory, and in the face of the last cited example and the weight of opinion adduced on the other side, make the further support of this theory at this time untenable.

*Summary.* A review of the evidence on the action of ferrous and ferric oxides in the vitrification of clay brings us to the following conclusions:

1st. The clay under discussion forms a black core normally, but seems abnormal in the fact that it also fuses in the red oxidized portions at about the same time, and both portions become nearly equally vesicular.

2nd. The same clay, after undergoing proper oxidation and having developed a dense red vitrified body, will form a blue vitrified body by reduction, which will swell from further heating at about the same time as the red unreduced portion.

3rd. Neither the red nor blue vitrified portions in either center or exterior swell until they have passed through a dense strong solid phase.

4th. Normal bricks studied in other instances seem to show a much wider temperature interval between the swelling of the black core and the swelling of the red portion from overfire.

5th. Evolution of gases in the vitrified mass is the ack-



nowledged cause of swelling, whether it be in red or black portions.

6th. Variation in the amount of gas-forming matter is suggested as the probable cause of the great apparent difference in the fusibility of the black and red portions, the black portion with much gas in it appearing more fusible than the red portion which still remains solid and unswollen.

7th. The question as to the difference in melting point of ferrous vs. ferric silicates is not settled by this evidence. Indications point to there being some difference, but a much smaller one than indicated by Wheeler; and that this difference is not the fundamental cause of the black coring reaction.

8th. The color changes in this clay do not strongly support the theory that the blue stoning reaction is caused by the increase in the proportion of ferrous oxide at the expense of the ferric oxide, and hence do not tend to weaken Seger's theory of the change of color by condensation of the volume of the iron.

9th. The figures obtained in this investigation do not strongly support the theory that the swelling during over-fire is occasioned by the dissociation of ferric oxide into ferrous oxide and oxygen, and much other evidence can be marshalled against this theory.

10th. The evidence altogether casts grave doubt on the state of oxidation of the iron being the cause of the black coring or swelling reaction.

## SULPHUR.

Sulphur may be present in a burnt clay as free sulphides of the metals like iron, or as such sulphides in solution in silicate slags, or as sulphates of the alkalies, earths or common meta's. The sulphides are not soluble in water, either when free or in solution in slags, but are usually easily dissolved by acids. The sulphates are easily soluble in water. Both of these forms, soluble and insoluble were determined, the latter by difference between the soluble and total sulphur.

*Methods of Analysis. Total Sulphur.* This was determined in the usual gravimetric way. A one gram sample was fused with dry sodium carbonate over an alcohol lamp, disintegrated in water, acidified with hydrochloric acid, evaporated to dryness and taken up with acid and water. The silica was filtered off, and to

the filtrate was added an excess of barium chloride. The precipitate was allowed to settle over night, was filtered off and washed first with dilute hydrochloric acid, and then with water containing a little ethyl alcohol. The filter paper was then charred and slowly consumed, and the precipitate finally ignited over a bunsen flame only when carbon had been pretty well burnt out. The crucible was then cooled, a couple of drops of sulphuric acid were added, and the crucible again heated till fumes of sulphuric acid ceased to come off. The precipitate was then weighed as barium sulphate and the sulphur calculated.

An alcohol lamp employed in fusing these burnt samples of clay was employed because alcohol is the only reasonably cheap form of sulphur-free fuel available in the laboratory. All artificial gases and natural gas contain it, and a sodium carbonate fusion cannot be made over a flame impregnated with sulphur, without some of it being taken up and thus vitiating the results. Sulphur-free alcohol is easily obtained. The construction of an alcohol lamp which could generate heat enough to make a hard fusion was a problem which had to be solved before we could proceed. The following device was found very convenient and entirely successful, although it is rather cumbersome and awkward in appearance:

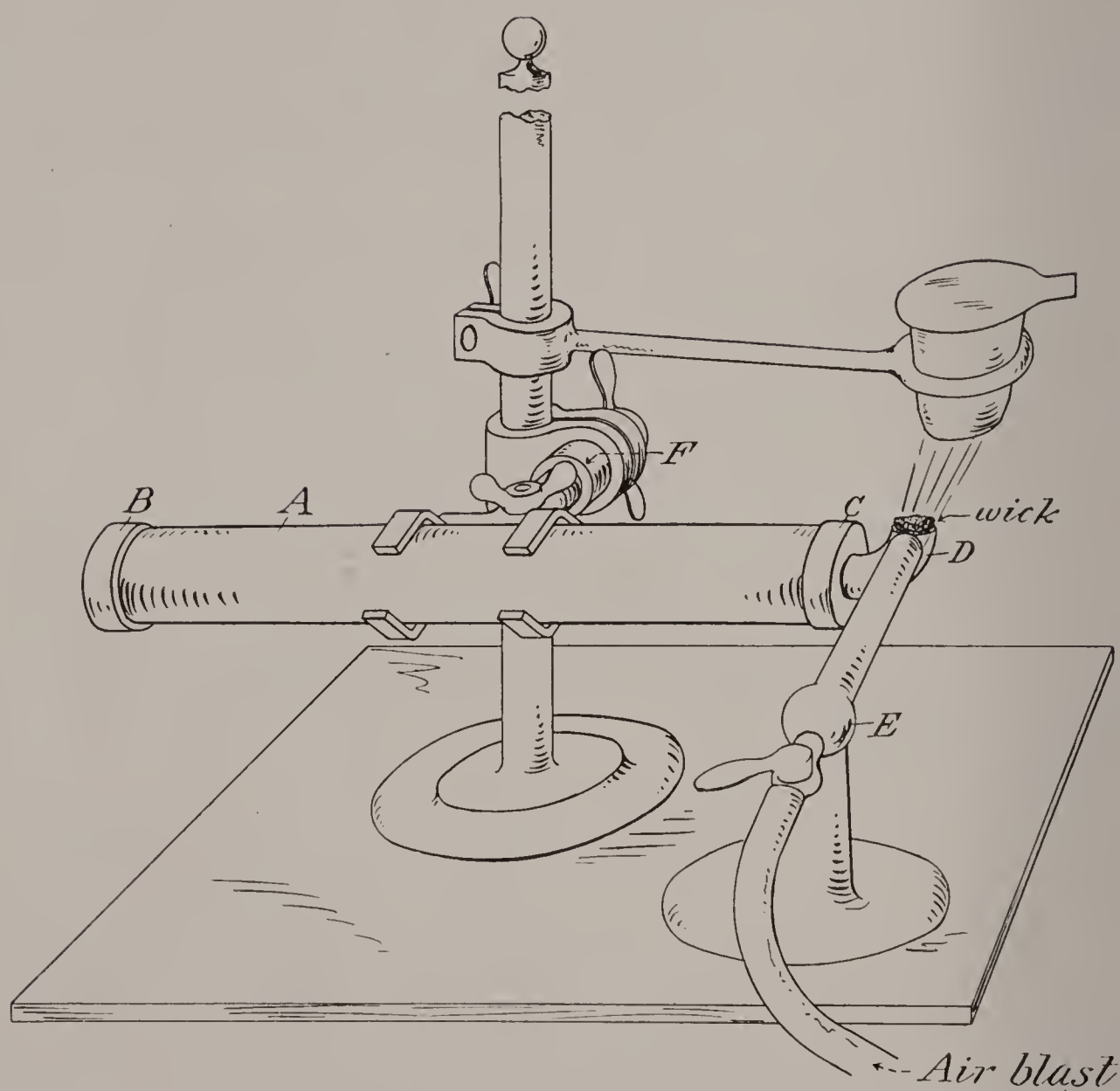


Fig. 24. Adjustable alcohol lamp for use with blast, in making fusions for sulphur analyses.



The reservoir of the lamp A is a piece of gaspipe  $1\frac{1}{2}$  inches in diameter by one foot long. It is capped at B, and at C is covered with a reducer which brings it down to half inch pipe. The tube through which the wick is inserted, D, is made of a one-half inch gas pipe nipple and elbow. These fittings are cheap and everywhere obtainable, and cannot be damaged by heating or upsetting or any other ordinary accidents. The wick itself is long and of large volume but very soft and unconsolidated, so as to permit very rapid volatilization of the alcohol. The wick runs back through C and extends well into A.

The lamp is mounted on an ordinary iron retort stand, held by a pair of large burette or apparatus clamps, of the double swivelled variety, which can be raised and lowered, moved in and out, and twisted on the horizontal axis as well. This clamp permits the lamp to be instantly adjusted in any position with regard to the blast apparatus E: The twisting motion is the most important, as it permits the lamp to be tilted so as to bring the alcohol to the wick at any rate desired. By tilting C up and B down around the axis F as a center, the alcohol must climb the wick for a long distance, and will hence support only a small flame. By tilting C down and B up, the alcohol can be brought to D under an actual pressure and the flame increased to any needed extent.

The above point is the only one of special convenience or value. Ordinary alcohol lamps will not give anywhere near heat enough for this fusion work, and this device made the fusion as easy as with gas. The blast lamp is used with air alone, and the nozzle placed almost touching the wick of the lamp and slightly above it. By this means, the flame is gathered up into a powerful jet or blowpipe flame.

In this sulphur work, it was necessary to exercise the strictest supervision of the chemicals used, because sulphates are the commonest impurities in chemical reagents. Blanks were run on everything, and every process was checked with accompanying blank determinations and the sulphur obtained from the water, air, and reagents was duly allowed for in the results. It was not possible to keep all sulphur out of the reagents, but they were kept as low as possible.

*Sulphur existing in form of Soluble Salts.* Two to five grams of the powdered sample were taken and heated, but not boiled, in

water made barely acid with hydrochloric acid. The water was decanted off into a calibrated flask at intervals of one to two hours, and replaced by fresh, until the last decantation gave no test for sulphates with barium chloride. The collected decantations were then diluted by filling the flask up to its calibration mark, and allowed to stand 12 to 18 hours. Then, by means of a pipette, an amount of solution corresponding to one gram of the original sample was removed. One or two drops of ferric chloride were added, then enough ammonium hydroxide to precipitate the flocculent ferric hydroxide. The iron carried the clay and fine mineral dust which had been carried along with it into the solution, down into the precipitate, which was easily filtered off. The perfectly clear filtrate was made acid with hydrochloric acid, and the sulphates precipitated as barium sulphate by an excess of barium chloride. The precipitate was allowed to settle and was ignited and weighed as in the case of the total sulphur.

*Insoluble Sulphur.* The difference between the total sulphur and that existing in soluble form is counted as insoluble sulphur.

*The Results.* The following table, No. 5, gives the results of the sulphur tests:

TABLE NO. 8. RESULTS OF SULPHUR DETERMINATIONS.

Designation of Burn.	Number of Draw-Trial.	RED PORTION OF BRICKETTES.			BLACK PORTION OF BRICKETTES.		
		Total amount of Sulphur expressed as the element.	Amount of Sulphur existing as soluble Sulphates, expressed as the element.	Amount of Sulphur existing as insoluble Sulphide, etc., expressed as the element.	Total amount of Sulphur, expressed as the element.	Amount of Sulphur existing as soluble Sulphates, expressed as the element.	Amount of Sulphur existing as insoluble Sulphides, etc., expressed as the element.
Raw	Clay	3.000 2.995	0.740 0.680	2.260 2.210	{ Calculated on basis of clay after dehydration loss of 11.16 percent.		
Burn A	1	0.940 0.950	0.835 0.842	0.105 0.108	2.40 2.39	0.210 0.160	2.190 2.230
	4	0.680 0.670	0.240 0.210	0.440 0.460	2.28 2.25	0.200 0.195	2.080 2.055
	7	0.530 0.520	0.096 0.096	0.434 0.424	2.15 2.12	0.164 0.157	1.986 1.963
	9	0.320 0.310	0.063 0.055	0.257 0.255	2.06 2.04	0.057 0.051	2.003 1.989
	14	No red in	portion this	produced sample	1.34 1.30	0.011 0.009	1.329 1.291
Burn B	21	0.290 0.280	0.051 0.051	0.239 0.229	{ These samples had no black core or black exterior.		
	22	0.270 0.260	0.050 0.044	0.220 0.216			
	25	0.234 0.217	0.045 0.044	0.189 0.173			
	28	0.220 0.213	0.027 0.025	0.193 0.188			
	29	0.172 0.172	0.023 0.016	0.149 0.156			
Burn C	37	0.213 0.207	0.030 0.030	0.183 0.177	0.266 0.255	0.030 0.016	0.236 0.239



*Discussion of the Results. The Determinations themselves.* The analytical results speak for themselves. The checks between duplicates average exceedingly close, and in no instance is there any wide discrepancy. The duplicates, and the orderly sequence of the changes shown between successive brickettes, all goes to prove that the work is accurate, or at least if any error exists it is a continuous error which does not vitiate the results for comparison purposes.

The absolute amount of sulphur present is very high—one of the worst cases which has come to our notice. Ordinary clay analyses do not report sulphur at all, but in the cases where it is determined, the amounts usually fall below one percent of sulphuric acid ( $\text{SO}_3$ ) or 0.40 sulphur (S).

*The Red Portion of Brickettes.* Observing this portion of the table, we see:

1st. That the sulphur experiences rapid expulsion in its total amount. At draw trial No. 1, taken at  $710^\circ$  after 17 hours, its quantity was only about 30% of the initial. At draw trial No. 9, taken at  $1100^\circ$  after 48 hours, the sulphur was only 10% of the initial. From here on, the losses dwindle and become very small. For instance, in Burn B, test piece 21, taken at 74 hours at  $1060^\circ\text{C}$ , the sulphur had come almost to the same point that it had reached in Burn A in 48 hours, and the losses in Burn B, up to the point where the clay became a spongy mass, floating on water, were very trifling. In this case, then, we may say that the loss of sulphur goes on under oxidizing conditions steadily, either with rising temperatures or with stationary temperatures, until the total residual sulphur is about 10% of the initial, after which its changes are slow and gradual.

2nd. The soluble sulphur, existing as sulphates if lime and other bases are first increased a little in the early stages of burning. Thus the soluble sulphur in the clay was 0.71 average, and 0.84 in the draw trial taken at  $710^\circ\text{C}$  (17 hours). The reason is not far to seek. The sulphides naturally oxidize to sulphates when treated with pure hot air, or if sulphur is expelled from  $\text{FeS}_2$  by dissociation at  $400^\circ\text{C}$  and the sulphur takes fire and burns to  $\text{SO}_2$  or  $\text{SO}_3$ , it is clear that it is held in the clay in part, by new combinations formed there.

3rd. The period when soluble sulphates are formed and retained unaltered in the clay is short, however, for at draw trial

4, taken at  $805^{\circ}\text{C}$ , 31 hours, there had been a heavy loss of soluble sulphur. Evidently the sulphates or sulphites formed are not very stubborn combinations, or they would not break down so easily. The soluble sulphates found from this point to the end of the third burn become less and less, and goes to show that the best method to overcome this salt in bricks and other architectural products is simply to heat them up to a point of moderate vitrification and hold them there.

4th. The insoluble sulphur, comprising sulphides and silica-sulphur compounds, undergoes some peculiar changes in the early part of the burn. Evidently, the heat absorbed below  $700^{\circ}\text{C}$  has powerfully affected the original combinations, for of 2.25% of insoluble sulphides in the clay, only 0.10% remains. Evidently, a large proportion of the sulphides are not only broken down but expelled also. A little is saved—enough to increase the soluble sulphates a little, but not much. But, after passing  $700^{\circ}$ , the conditions are reversed. The sulphur remaining at that time is mainly soluble in water, but heating to  $800^{\circ}\text{C}$  renders it again insoluble.

Thus, the 0.10% at  $700^{\circ}\text{C}$  becomes 0.44% at  $800^{\circ}\text{C}$ , and part of this must have been derived from the 0.84% soluble sulphur at  $700^{\circ}\text{C}$ .

From  $800^{\circ}\text{C}$  on, this residual sulphur hangs on doggedly, and is expelled only a little at a time, and apparently time is more important than temperature in getting rid of it. Nearly all of the residual sulphur from  $800^{\circ}\text{C}$  is of the insoluble form. It would be interesting to know what the form is, but we have only hypotheses to offer. It may be sulphides held in silicate solutions, like the matter produced in smelting many ores. There is no question of the ability of silicate slags to dissolve and hold sulphides in themselves, or at least to disguise their presence so that they are not detected by the eye as a foreign ingredient. There is also no question but that sulphates, or sulphuric acid, is soluble in silicate slags and glasses. Either of these forms would hang on to their sulphur well, and probably would not give them up without the interference of some new reaction—other than air oxidation.

These changes in the sulphur content are well shown in the following curves:

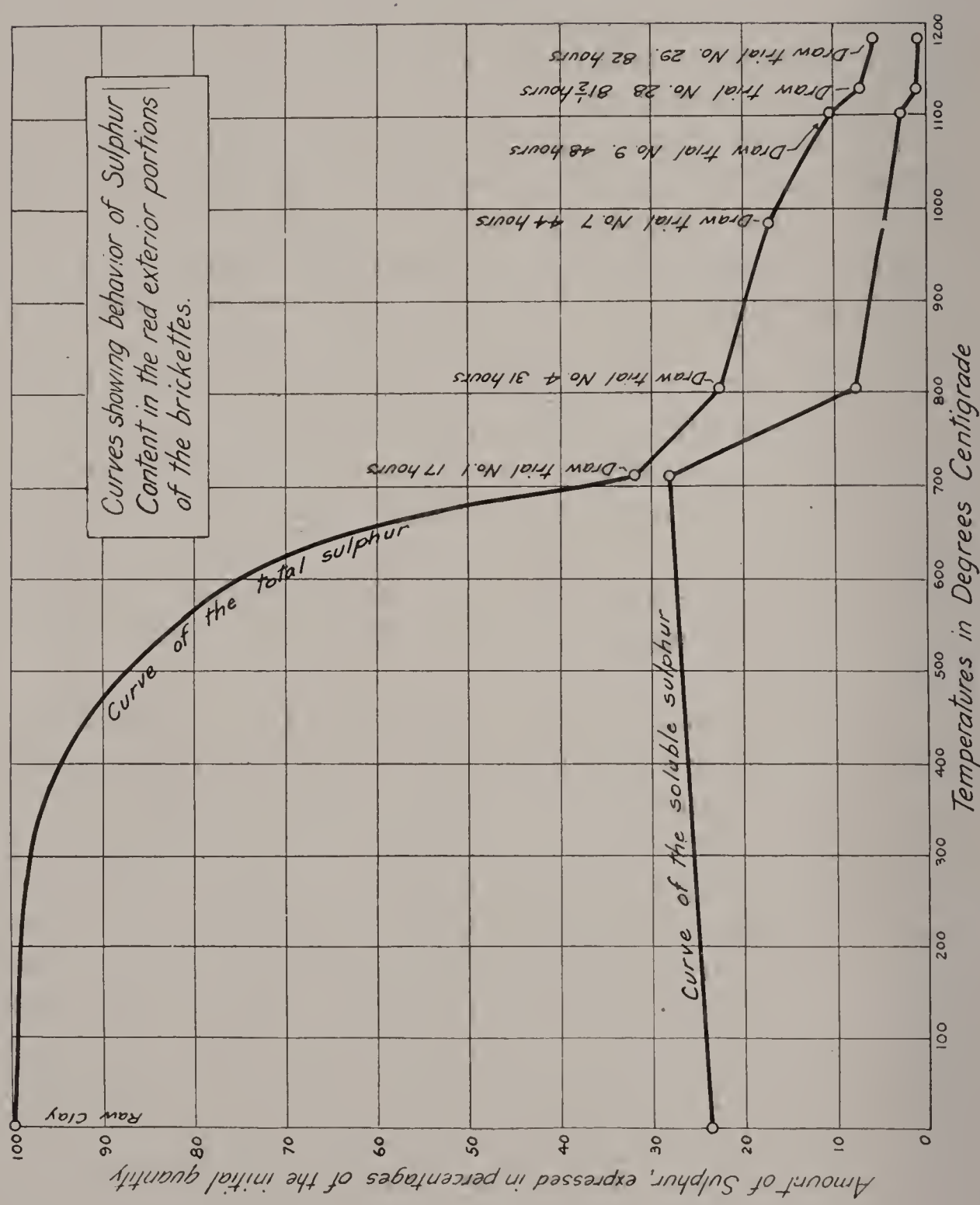


Fig. 25.



The preceding curve is drawn in such a way that the course of the determinations is shown but that, if the whole area of the curve sheet be considered to represent all of the sulphur of the clay during the whole time of the test, then

The area A. A. A. represents the quantity expelled.

The area B. B. represents the insoluble sulphur remaining.

The area C. C. represents the soluble sulphur remaining.

The areas B and C together represent the total sulphur remaining.

These areas show beautifully by their size and shape the various events and situations, especially the increase of the soluble sulphates for a time and their succeeding rapid diminution.

*The Black Portion of the Brickettes.* Observing this portion of Table No. 5, we find a very different state of affairs:

1st. The total sulphur drops away slowly and reluctantly, having at the advanced stage of brickette No. 9 (48 hours,  $1100^{\circ}\text{C}$ ) only lost about 30% of its initial quantity. When pushed up to strong vesicular fusion, the rate of loss increases, but even then nearly one half of the sulphur remains.

2nd. The soluble sulphur follows the same general course in the black portion as in the red, with the important exception that it shows no marked increase in the lowest temperature ( $700^{\circ}\text{C}$ ) trial piece. This indicates that the cause of the marked increase of soluble sulphur in the red exterior portion is due to the oxidation of the sulphides to sulphates, while in the black interior, oxidation of the sulphur would not be likely to occur while carbon was present and still unoxidized. Thus in draw trial No. 1, we have 0.84% soluble sulphur on the outside, or more than the raw clay contained, while we have 0.185 on the inside; in the outside, we have 88% of the sulphur present, in the soluble form, while in the inside we have 2.5 times as much sulphur present, and of this only 7.7% is soluble.

These figures sufficiently prove the entire reversal in tendency brought about by the presence of the carbon. It seems not only to have delayed the expulsion of the sulphur from the clay, but it seems to have reduced to some extent the sulphates back to insoluble sulphides. After the heat begins to rise ( $800^{\circ}$  and above) the soluble sulphur is reduced steadily to vanishing quantities, very much as in the exterior, though proceeding a little faster all the way along.

3rd. As a natural corrolary to what has preceded in 1 and 2, the insoluble sulphur in the black portions remain high throughout—nearly up to the total. This simply emphasizes the fact that the sulphides in the center are protected from oxidation, both by their location and by the surrounding carbon, and this enables them to stand comparatively high temperatures with but little loss.

4th. When the clay has been pretty completely oxidized and the sulphur expelled by normal processes, the application of a heavy reducing atmosphere, which undoubtedly contains some sulphur, may cause re-absorption of sulphur. In this case, there was a small but clearly marked increase in the exterior of the ware. Thus the blue black exterior of sample 37 contains 0.266, while the red and unreduced interior contains only 0.210.

The relationships between the total and soluble sulphur in the black cores are well shown in the following curve:

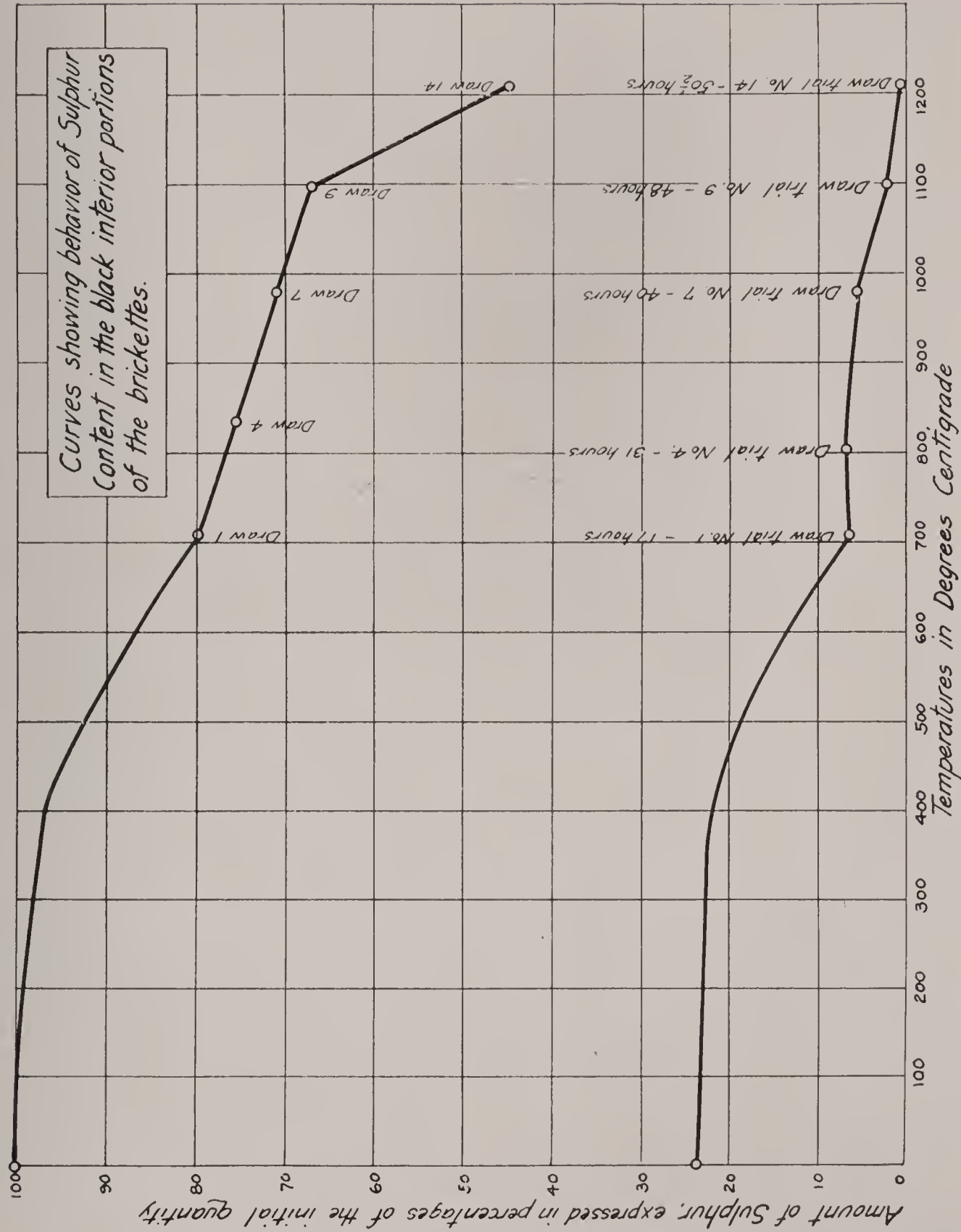


Figure 26.



This curve is drawn so that it divides the field up into areas proportional to the amounts of sulphur in the various forms during the progress of the test.

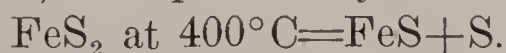
The area A. A. represents the amounts of sulphur expelled from the center of the clay in burning, from the beginning up to vesicular fusion and the formation of a sponge.

The area C. C. represents the amount of sulphur existing in the soluble condition during the range of the test.

The large area B. B. B. indicates the amount of sulphur which is held in insoluble form in the clay through the action of the carbon in the core.

*The Reactions by which Sulphur is Expelled.* There are probably a number of ways in which sulphur may be expelled during the burning process. Only some of the simpler ones, of whose operation there can be little doubt, will be given.

*The Normal breaking down of Pyrite.* Pyrites, when heated, suffers decomposition, as expressed by the reaction



The free molecule of sulphur distills off as such, as can easily be verified by conducting the operation in a closed glass tube, where it can be kept free from air. When conducted in the open air, the S immediately catches fire and burns to  $\text{SO}_2$  or  $\text{SO}_3$  instead of depositing as a coating or crystalline fibre on the sides of the glass. When it occurs in a clay, at some distance beneath the surface, the action resembles, to some extent, that of the closed glass tube, in that air finds trouble in reaching it at once. But the conditions differ from those in the glass tube, in that the surrounding body is spongy, and allows gases under pressure to make their way out in all directions, and the clay being hotter as the surface is approached, there is little or no likelihood of the sublimate recondensing on its outward journey.

The outgoing sulphur fumes are very apt therefore to pass over the bases, some of which have been newly relieved from  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc., and are ready for or susceptible to attack by the sulphur. Iron ( $\text{FeO}$ ), lime ( $\text{CaO}$ ) and magnesia ( $\text{MgO}$ ) all are liable to this kind of attack.

There can be no doubt, however, that the bulk of the sulphur from  $\text{FeS}_2$  broken up in the clay, escapes with the waste gases and the clay is relieved of it.

2nd. *The Slow Oxidation Process.* After  $\text{FeS}_2$  has broken

down, and lost one half of its sulphur, the remaining FeS would oxidize in the air, if given a chance, at temperatures of  $400^{\circ}\text{C}$  and above. But this condition seldom lasts long, for the clay usually is pushed rapidly along to incipient vitrification, and its air supply grows steadily less as its pores contract and become choked and discontinuous. Thus in figure 25, the course of the total sulphur curve from 0 to  $700^{\circ}\text{C}$  illustrates the operation of the first reaction, or the breaking down of the pyrites, beginning at about  $400^{\circ}$  and losing 70% of the sulphur in the next  $300^{\circ}$ . The second reaction, or the roasting out of the sulphur from the FeS is illustrated by the curve from 700 to 1100. Here the rate of loss is slow and fairly regular, and it is shown that mere heating up of the clay in oxidizing atmosphere is not sufficient to drive out all of this residual sulphur in any reasonable time. Further, the removal of sulphur from FeS cannot be accomplished by heat alone, for the substance is readily fusible, at about  $1000\text{--}1100^{\circ}\text{C}$ , and when fused is readily taken into solution in silicate combinations.

3rd. *The Dissociation of Sulphates.* Ferrous sulphate in oxidizing atmosphere loses its sulphuric acid ( $\text{SO}_3$ ) rapidly and fairly completely at a temperature of dull redness— $550\text{--}650^{\circ}\text{C}$ . The product, the ferrous oxide, promptly changes to ferric oxide, producing the material familiarly known in the paint trade as Venetian Red. The color of the oxide varies with the temperature at which the decomposition takes place. It is brightest red at the lowest temperature, and grows darker, till it becomes purple and almost violet-black at high temperatures. The last 2 per cent or so of sulphuric acid sticks obstinately, and cannot be expelled without heating the material so high as to spoil its bright red color. Hence, commercial Venetian red is ordinarily impregnated with sulphate of iron, which causes it to make trouble when used as a mortar color.

Calcium sulphate also breaks down, but at considerably higher temperatures than ferrous sulphate, and less completely.

It is probable that the intervention of reducing conditions are necessary to effect a satisfactory decomposition. No case of  $\text{CaSO}_4$ , breaking down with evolution of visible  $\text{SO}_3$  has come under the writer's observation, but cases of breaking down with copious evolution of  $\text{SO}_2$  have been witnessed, and under conditions which made the explanation of the source of the reducing



agent or action very obscure. The use of  $\text{CaSO}_4$  in porcelain and  $\text{Na}_2\text{SO}_4$  in the batch for glass manufacture is always in connection with reduction as a means of expelling the sulphur.

On observing the curve sheet, Fig. 25, it is seen that the sulphates, represented by the curve of the soluble sulphur, increase in amount up to  $700^\circ\text{C}$ . While the sulphur as a whole has decreased 70%, the sulphates have increased 16%. Immediately after  $700^\circ\text{C}$ , however, the very abrupt fall in the line shows that some of the sulphates are decomposing—probably the  $\text{FeSO}_4$ .

About 75% of the sulphates are broken up and expelled during the next  $100^\circ\text{C}$ . The remaining 25%, probably comprising the calcium sulphate chiefly, are expelled steadily but slowly, so that a small amount remains still after the clay has fused to a sponge.

*Influence of Carbon and Iron.* It appears from a study of Figure 26, that the central portion of the clay gave up its total carbon very slowly, and that the proportion of sulphates was not increased by oxidation in the early part of the burn as in the outside parts, and that the bulk of the sulphur in the clay remained there, in insoluble form, until about  $1100^\circ\text{C}$ .

Since these events are so diametrically opposite to what occurred in the exterior, or carbon-free portion, and since no other known cause of variation between the inner and outer portions existed, we are compelled to conclude that the carbon has been responsible for this change. The mode of its action is not known and can only be conjectured.

In order to bring these relationships more clearly into view, the following curve sheet, Figure No. 27, has been prepared:



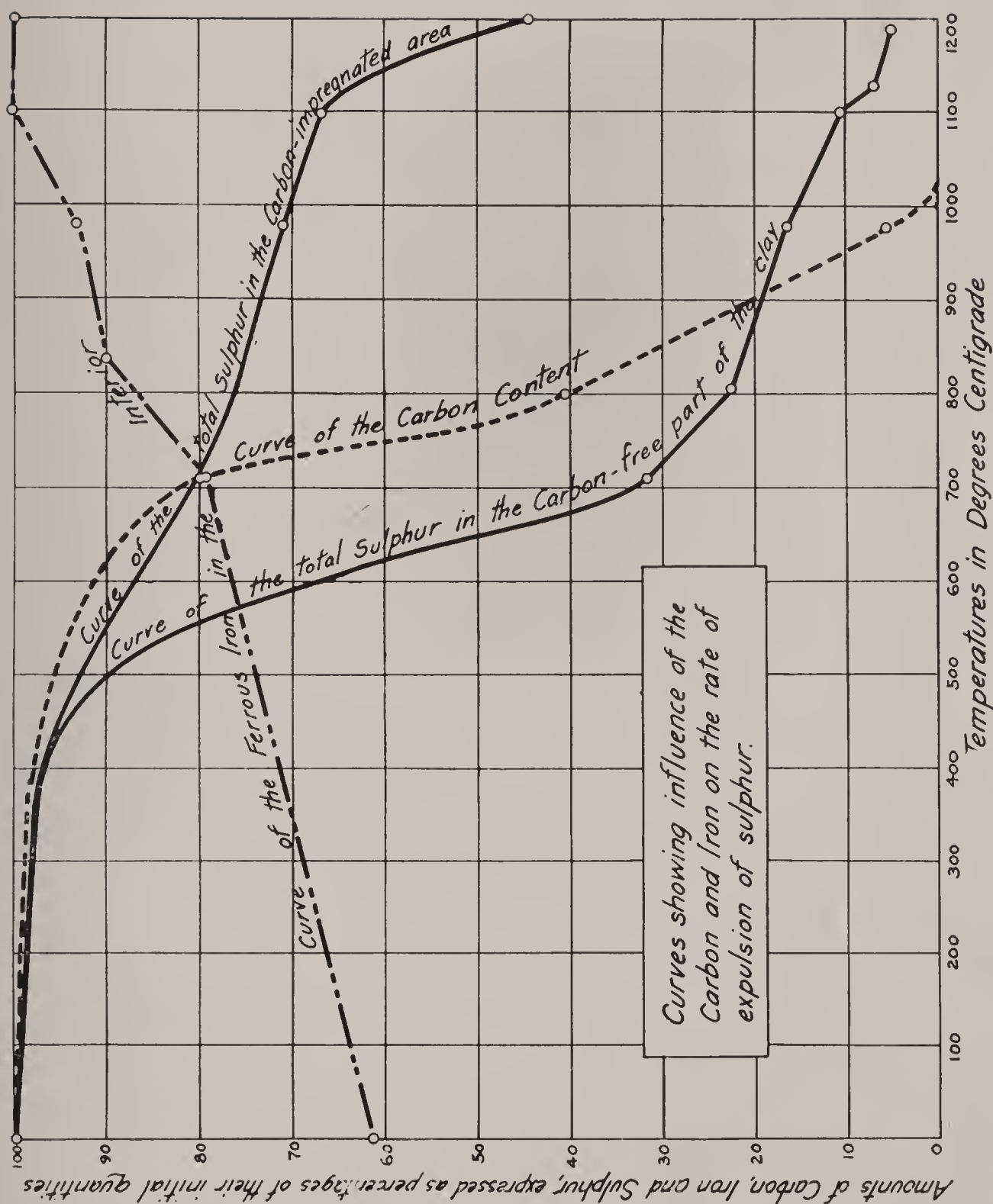


Figure 27.

From this figure, it is seen

1st. That both carbon and interior sulphur have lost 20% up to 700°C. That exterior sulphur has lost 68% in the same period.

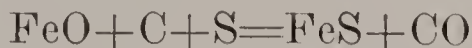
2nd. That carbon continues to lose rapidly, until all is gone at about 1000°C.

3rd. That at 1000°C the interior sulphur has lost an addition at 6 or 8%, while the exterior sulphur has lost about 90%.

4th. That the sulphur of the interior soon after 1000°C begins to be expelled at a much more rapid rate, while the rate at which the sulphur of the exterior escapes remains unaffected by the expulsion of the last of the carbon.

On the other hand, it must be allowed that the physical factors in the case probably are exerting some influence, and are co-responsible with the carbon for the late expulsion of the sulphur from the interior. The last of the carbon disappeared at about 1000°C, but the rate at which the sulphur was expelled *did not at once change*. Doubtless, the difficulty of oxygen getting at it is responsible for this fact, for the clay at 1000°C is so dense that gases could only get in or out slowly and with difficulty.

It may also be asked, *how* does the carbon act upon the sulphur compounds to restrain their expulsion. The most natural hypothesis is that when  $\text{FeS}_2$  is broken down into  $\text{FeS}$  and  $\text{S}$ , the free sulphur instead of being expelled, as is the case in the exterior, combines with the ferrous oxide present, forming  $\text{FeS}$ . The iron, as shown on the curves (see figures 22 and 23) begins with 62% in the ferrous form, probably mostly ferrous carbonate. From results of an incomplete test, made in 1902,\* we know that ferrous carbonate breaks down and gives up its  $\text{CO}_2$  as low as 425°C, by the reaction:  $\text{FeCO}_3 + \text{heat} = \text{FeO} + \text{CO}_2$ . If meanwhile, free sulphur is liberated in its immediate vicinity, and in the presence of carbon, the reaction



would be likely to occur. The probability of this is increased from the study of the curves Fig. 27, where the carbon is rapidly expelled, while the ferrous iron increases and the sulphur remains almost in statu quo.

Inasmuch as the chart, Fig. 27, is constructed so as to show

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\*Trans. Am. Cer. Soc., Vol. V, p. 400.

the three reagents as percentages of their initial quantities, the point naturally arises whether the actual quantities present are sufficient to make the above reaction quantitatively possible. A calculation shows that they are; even after allowing for the losses of carbon at various points in process, there is always enough left to more than accomplish the dioxidation of the iron as shown.

Thus a logical and entirely plausible explanation of the slow removal of the sulphur from the dark core or interior portion of the brickettes is shown in the conversion of the sulphur into the form of ferrous sulphide,  $\text{FeS}$ , by the joint cooperation of the ferrous oxide and free carbon. As has already been explained, ferrous sulphide once formed can not be broken up by mere heat. It must be either decomposed by roasting in air, or by the reactions to be next described.

*Expulsion of Sulphur by Silicic Acid.* It has long been known that at high temperatures silicic acid becomes a very active acid, displacing all other common acids, and combining with their bases to form silicates. In this way it has the power to replace sulphuric acid, and the sulphur of sulphides.

Seeger\* found that a bisilicate glass mixture, saturated with sulphates, showed a sulphuric acid content of 4%, while the same glass with one extra molecule of silica added and melted in at the same temperature and under the same conditions gave a glass which showed a sulphuric acid content of only 2%. From this he drew the conclusion that a bisilicate mixture saturated with sulphuric acid when changed to a trisilicate by taking up silicic acid, discharged 2% of its sulphuric acid in the form of sulphurous acid and oxygen.

It is a fact of great commercial importance in blast furnace practice that a basic slag, that is, one low in silica, will absorb sulphur, but that an acid slag, that is, one high in silica, will give off sulphur.

These two samples go to show that as long as a fused silicate mixture is quite basic in character, sulphur will not be affected, but, as the mixture becomes more silicious, the silicic acid will tend to replace either sulphuric acid or the sulphur of a sulphide.

The first stage in the vitrification of a clay ware is the formation of a fusible matrix in the interstices of a less fusible skeleton. We do not know the constitution of this matrix, nor

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\*Collected Writings, page 646.



is it likely to be the same in different cases, but we have had a general idea that it consists in the greater part of the more fusible fluxing bases, with a small amount of silica.

Of late years, scientists have carried on a considerable amount of study regarding the properties of fusing slags and silicate mixtures, and have given a new name to the most fusible combination possible at any given temperature with a given set of ingredients. They call it a "Eutectic." The action of the eutectic is selective; that is, the various ingredients in a mixture do not go into solution in the proportion in which they are present, but in the proportion in which they are needed to make the most fusible mixture possible. It has been found that the eutectic is always very basic at low temperatures, and becomes more acid as the temperature rises.

Keeping the two statements in mind: first, that as a silicate fusion becomes more silicious it will drive off sulphur; second, that the fused matrix of a clay is a basic silicate mixture, gradually becoming more silicious as the temperature rises, we can easily understand the swelling and marked vesicular structure developed in our samples.

(a) Sulphur was present in the samples, as we know from the analyses.

(b) The samples reached vitrification without puffing, as is seen by inspection of the trial pieces.

(c) The fused matrix in these vitrifying brickettes was a basic silicate mixture, gradually becoming more silicious—the study of eutectics in other connections has shown that this is always the case.

(d) When the matrix became silicious enough, silica would have begun to drive off the sulphur; experience with other silicate mixtures has shown that it should do so, and the analyses show that in this case there was a sudden and marked change in the rate of sulphur expulsion between 1100° and 1200°C. Moreover, this change of rate is apparent in both exterior and interior parts of the brickettes, and therefore seems to be independent of the former causes of sulphur elimination.

The exterior portion lost but little actual weight of sulphur between 1100 and 1200°C, but it lost nearly 50% of what there was present. The interior portion lost a large amount of sulphur,

amounting to one-third of the amount present, or nearly as much as had been lost in the 1000°C preceding.

(e) The reactions by which the silicic acid ousts the sulphuric acid or sulphur from sulphates and sulphides, are not definitely known. They may be something like the following:

In the oxidized portions of the sample where most of the sulphur was present as sulphate:



where M is any bivalent base, or

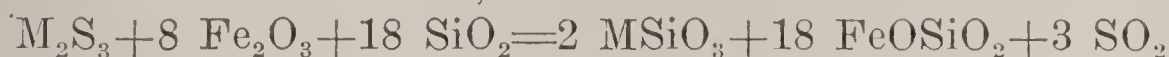


where M is any trivalent base.

In the black cores which had never been oxidized, and in the portions that had first been oxidized and then heavily reduced, as the exteriors of draw trials No. 37 to No. 40, the sulphur was in all probability in the sulphide form (FeS), and the reaction might run like this:



where M is a bivalent base, or



where M is a trivalent base.

The reactions, when they take place in a brick, are no doubt a great deal more complex, but the suggestion given shows the fundamental reaction in puffing, namely, the setting free of  $\text{SO}_2$ .

On consulting the curves, Fig. 27, it is seen that in this case, while the suggested reactions could easily have taken place in the red exterior portions, where  $\text{Fe}_2\text{O}_3$  was in abundance, they could hardly have done so in the black interior, because all of the iron present was already present as ferrous oxide. This is by no means a bar to the successful operation of the theory, for it is entirely possible that ferrous oxide might be reduced still further to Fe, by sulphur disengaged at this high temperature. It is also possible that other oxides may give up oxygen under the pressure of the increasing activity of the silicic acid.

(f) The rapidity of the evolution of the gas  $\text{SO}_2$  in both interior and exterior portions was sufficient to cause the hitherto apparently sound structure to become highly spongy—in fact, so light as to float on water. No other gases of which we have knowledge were disengaged at this time. Water was long ago eliminated. Carbon was all expelled at 1000°C and the clays

had not yet swollen markedly, so that it seems that carbonic acid or carbonic oxide could scarcely be the actuating cause.

(g) The volume of the sulphur dioxide ( $\text{SO}_2$ ) given off is easily able to account for the sudden and extraordinary swelling shown by this clay, as is shown by the following computation:

Taking samples 25 and 29, from the exterior portion of the brickettes which cover the observed period of swelling, and examining their sulphur contents, we find:

No. 25. 0.0023 gram sulphur in 1 gram sample

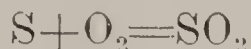
No. 29. 0.0017 gram sulphur in 1 gram sample

— — —

0.0006 gram sulphur lost during swelling

1500.0000 grams is the weight of the brickette, and assuming that the whole of it was affected by the swelling, we would have  $1500.0000 \times .0006 = 0.9$  grains of sulphur lost by swelling.

When  $\text{SO}_2$  is formed the reaction is



or, by weights:  $32 + 32 = 64$

Hence  $0.9 \times 2 = 1.8$  grains  $\text{SO}_2$  produced.

1 liter of  $\text{SO}_2$  at  $0^\circ\text{C}$  and 760 m.m. pressure weighs 2.785 grams\*.

1 liter of  $\text{SO}_2$  at  $1100^\circ\text{C}$  and 760 m.m. pressure, would weigh 0.5261 grams.

$1.8 \div 0.5261 = 3.4$  liters, volume of  $\text{SO}_2$  formed from the oxidation of .0006 grams sulphur at  $1100^\circ\text{C}$ .

1 liter = 61 cubic inches. 3.4 liters = 207.4 cubic inches.

The volume of the brickette was  $2\frac{1}{2} \times 3\frac{7}{8} \times 3\frac{7}{8} = 37.5$  cubic inches.

$$207.4 \div 37.5 = 5.5$$

That is, the volume of  $\text{SO}_2$  that would be generated would be 5.5 times as large as the whole sample. Even if the pore space left in the brick were 10% of its volume, the volume of gas would be 55 times as large as the space available.

As the volume of a gas varies inversely as the pressure, when the temperature remains the same, to calculate the pressure that would have been exerted by this gas, if it had been held in the available space, we use the formula

$$\text{Atmos. pr. } 14.7 : X :: 1 : 55 = 808.5 \text{ pounds per sq. in.}$$

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\*Smithsonian Physical Tables.



Thus we see that a very small actual weight of sulphur may well cause puffing if it gets oxygen for combustion, or if it is forced out of a solid compound and into a gaseous state at this high temperature, and surrounded by a viscous and but slightly porous body.

*The Interstitial or Residual Gas Theory of Swelling.* Another explanation of the swelling of clays recently set forth by Purdy and Moore\* shows that the gases filling the interstitial spaces in the gradually vitrifying clay structure, and which are cut off from escape by the fusing of the walls of the pore channels, tend to convert the irregular shaped cavities in which they are imprisoned into spherical cells, exactly as a glass blower converts a shapeless mass of glass into a sphere by expanding the gas in the center by blowing it. The development of a vesicular structure from this cause is undoubtedly possible, and in fact normally to be expected whenever any silicate mass is brought to a condition of viscosity by heat. But there is a marked difference between the development of a vesicular structure from this cause, and that brought about by the sulphur in the present instance, for the latter was so very quick in its development and the sponginess produced was so exaggerated, while ordinary bloating from over-fire develops gradually from very small beginnings. In fact, it was shown† that vesicles were forming in the glassy matrix at temperatures far below the point of complete vitrification and while the structure as a whole was still porous. The swelling is due in this case to the simple change of volume of a gas by heat, while the sulphur reaction arises from the sudden conversion of a solid into a gas, after the clay has already assumed the vitreous structure.

If the facts and deductions concerning this sulphur silica reaction are correct, the question may well arise, why are not clay wares more generally swelled from its operation? Clay wares of the common sorts, especially those made from shales and fireclays, generally contain either sulphides or sulphates or both, and in amounts larger than the small quantities dealt with in paragraph (g). Iron and carbon also are common impurities.

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\*Pyrochemical Properties of Clays, Volume IX, Trans. Am. Cer. Soc.

†Ibid.

To this, it may be answered that the bulk of the shales and many of the fireclays do break down with a scoriaceous structure from over-fire—in not infrequent cases, as badly as the sample used in these tests. It requires, however, the combined presence of all three impurities, to develop the trouble at its worst. Also, in the case of clays containing small quantities of the troublesome ingredients, the reduction in quantity of the reagents before vitrification takes place may reduce the tendency. Also, clays with opener texture, or clays with later melting point, would probably evade the difficulty by permitting the gases to escape. The thickness of the cross section is also of much importance, as a thin cross-section permits oxidation clear through the body much more easily.

*Summary.* A review of the evidence on the influence of sulphur brings us to the following list of conclusions:

1st. Both sulphates and sulphides experience rapid diminution by dissociation, in that portion of the burn up to  $800^{\circ}\text{C}$ , in those portions of the ware which get air freely. This loss of sulphur may amount to two-thirds or three-fourths of the amount originally present.

2nd. Both sulphates and sulphides experience a further slow diminution by dissociation or oxidation, beginning at  $800^{\circ}\text{C}$  and continuing as long as the clay structure remains porous and permeable to air. The loss of sulphur may amount to 90% or more of the initial sulphur content at the end of the period, but it proceeds increasingly slowly, and probably would never become complete.

3rd. In the interior portions of the clay, where air penetrates with difficulty, the reactions of paragraphs 1 and 2 may be greatly modified. The loss of sulphur will be much less, and if there are bases present with which free sulphur may combine, as  $\text{FeO}$ ,  $\text{CaO}$ , or  $\text{MgO}$ , there is strong likelihood that the sulphur will not be expelled.

4th. The presence of carbon, even in small quantities, interferes still more strongly with the expulsion of sulphur in any form, and the sulphur will not suffer much loss until after the carbon has been expelled. In many cases the clay has become too dense by that time for oxidation of the sulphur to proceed, so that the carbon has virtually prevented its escape.



5th. The retention of sulphur in any form and from any cause in the mass of the clay is not likely to cause physical disturbances in the clay until a fairly complete degree of vitrification has been reached.

6th. When a clay reaches a dense vitrified condition, it proceeds normally, after a longer or shorter interval, to become less dense, by reason of the development of multitudes of minute vesicles in the viscous body; this process is progressive and in the end, the body becomes spongy, weak and worthless.

7th. The length of this period of dense vitrification is much shortened, and in some cases practically abolished by the presence of sulphur compounds, which break down and evolve gases copiously, producing a prematurely spongy body.

8th. The cause of this gas evolution is chiefly the dissociation of sulphides and sulphates by silicic acid, which becomes increasingly active as the temperature rises, and appropriates the bases formerly combined with the sulphur.

9th. In clays of low sulphur content, and of favorable structure for oxidation, the amount of sulphur left in the clay at vitrification is very small. Hence the period of good structure is long, the vesicular structure develops slowly, and the clay is said to stand over-firing well.

10th. In clays of high sulphur content, or of dense structure unfavorable for oxidation, or of high content of iron and carbon, the escape of the sulphur is prevented, the clay has a very narrow period of usefulness or none at all, and the vesicular structure becomes enormously exaggerated.

11th. While this premature and exaggerated swelling from sulphur may in bad cases occur in well oxidized clays, it is practically certain to occur where clays containing a partly oxidized core are allowed to reach the vitrification period.

12th. This breaking down of sulphur compounds by silicic acid, is the chief or common cause of the premature swelling of black cored clays, and the occasional cause of sudden and severe swelling of properly oxidized clay wares.

13th. The proper way to avoid the effects of sulphur in vitrifying clay bodies, is to apply a deliberate and complete oxidation treatment, while the clay remains porous. This will rid the



clay of the greater part of the sulphur, and will prevent sudden or premature slagging of the clay by ferrous oxide, if it is true that ferrous oxide has such a tendency, and will thus avoid, so far as possible, the conditions which favor the swelling. Clays which still give trouble from swelling after this treatment must be regarded as bad clays.

### GENERAL CONCLUSIONS.

In the foregoing pages, the behavior of each of the three prime impurities of a clay, if we may so characterize them, has been subjected to as careful a scrutiny as the data itself warrants. Certain tendencies or modes of action have been strongly indicated by this data, and these tendencies, while by no means to be taken as final truths from the testimony of this one clay—a clay which it must be freely admitted is extraordinary—nevertheless foreshadow the lines of action which we should expect from the same materials in other clays. Until more and better data is at hand, therefore, we are justified in provisionally using these principles as laws on which to base our future interpretations of the composition and resultant properties of clays. Only by the verification of these laws by the application of similar methods to other clays of diverse character, can they assume real or lasting acceptance. The following are the deductions which the data here presented seems to most strongly support:

I. The black-coring of clays is a complex process, which has its origin and development in the following series of overlapping chemical steps or stages:

#### *Black-Coring.*

(1) Carbon, bituminous matter or organic matter of some sort, is a very common, and in fact almost universal component of clays.

(2) On being heated in a clay, it tends to burn out. Owing to the physical structure of the clay, the retarding influence of water in the clayware, the retarding influence of kiln atmosphere low in oxygen or high in reducing gases, the shortness of time allowed, or some other agencies, this burning out is often delayed and the clay reaches a strong red heat without being completely freed from this material.

(3) When the carbonaceous matter escapes oxidation until temperatures of visible redness in daylight are reached, it tends to undergo a destructive distillation, by which a portion is expelled from the clay in the form of light highly combustible gases, which are likely to ignite and burn furiously in the kiln, and thus make the situation worse by raising the temperature still higher and more rapidly. If the air supply is restricted, by closing doors and air intakes, and the gas is allowed to smother or only partly burn for lack of oxygen, the temperature may be controlled and kept below the danger point of  $900^{\circ}\text{C}$ .

(4) The residue of the carbon of the clay, called the fixed carbon, after the expulsion of the volatile matter, is in the condition of coke, or graphite, or charcoal, deeply ingrained into the structure of the clay by the process of distillation. The clay is like a sponge permeated by a volatile liquid, which decomposes, leaving a residue in every part of the mass. This carbon, being non-volatile and more or less dense, cannot be removed except by oxidation. Mere heating is not sufficient.

(5) This carbon may be removed by oxidizing with air, at comparatively low temperatures. This is the proper way, but it takes time—sometimes a long period—and burners often become impatient and proceed without waiting for the safe time. This must be done below  $900^{\circ}$ , while the clay still remains spongy and permeable to air going in and the resultant products of oxidation going out. If the clay is heated beyond this point, it is apt to become so dense that oxidation from outside ceases.

(6) The carbon may be removed by contact with other reducible materials, such as metallic oxides like  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ , or acid oxides like  $\text{SO}_3$  or  $\text{N}_2\text{O}_5$ . In this case, the resultant gases are liberated in the clay and strive to make their way out, probably under pressure. The temperature at which the fixed carbon is oxidized by contact with  $\text{Fe}_2\text{O}_3$  or  $\text{SO}_3$ , etc., is not definitely known, but it is not far from  $1000^{\circ}\text{C}$ . At the temperatures at which it occurs, few clays if any are so dense as to prohibit the escape of the resultant gases. Consequently, there is little likelihood of fixed carbon remaining in a clay until vitrification is reached unless the amount is excessive and more than can be oxidized by the reduction of any ferric oxide or sulphates present.

(7) Carbon is a possible but rare actual cause of the dark coloring of the core of clays unsufficiently oxidized. It is very



doubtful if the escape of the oxidized carbon is a possible actual cause of the swelling or vesicular structure of clays.

(8) The iron found in clays tends in the absence of carbon or sulphur to oxidize easily to ferric oxide. In the presence of carbon or sulphur, this oxidation is not possible until the bulk or whole of these substances have been oxidized. In fact, the evidence indicates that the iron oxide itself usually accomplishes a part of the oxidation, and is itself left in the magnetic, or ferrous, or even spongy metallic condition.

(9) The iron thus reduced is not likely to be again easily oxidized, because the increased density of the clay constantly reduces the circulation of air through its structure. Consequently it is highly likely to be taken into silicate combination as vitrification proceeds, while still in the lower stages of oxidation, and in this case imparts black or dark colors to the clay.

(10) The view has long been held that the presence of iron in lower forms of oxidation than  $\text{Fe}_2\text{O}_3$  is a powerful agent in slagging the clay at much lower temperatures than if the clay contained iron only in the  $\text{Fe}_2\text{O}_3$  state. This evidence does not support that view, there being but little observable difference in fusion temperature of the oxidized and unoxidized portions, though the latter were undoubtedly the first to show signs of fusion.

(11) The black coloration of the unoxidized cores of improperly fired clay wares is usually chiefly or wholly due to the formation of ferrous iron silicates in the clay.

(12) The formation of ferrous silicate in the cores has not been shown to have been accompanied by the evolution of gases or the immediate swelling of the ware. Evidence has been collected tending to show that perfectly quiet combination between iron and clay may take place without development of any swelling.

(13) The sulphur of the clay, in whatever form it originally occurred, is subjected to partial expulsion by the mere rise in temperature of burning, but it cannot be wholly or even principally expelled by heat alone. By the same oxidizing treatment by which the carbon is removed, sulphur is greatly reduced but never wholly expelled. Sulphur oxidizes *after* the carbon however, and hence where any carbon still remains, the sulphur can not be seriously reduced in quantity.



14. Sulphur in any form may give rise to gases at high temperatures in the clay, by oxidation or dissociation, or by substitution by silicic acid. These reactions are practically certain to take place in any clay at some point in its vitrification range, and when they take place, they cause swelling and vesicular structure to develop.

(15) Since the unoxidized portion of the clay contained carbon longest, its content of sulphur will be less reduced by the action of heat, and its potential capacity to give off gases will be greater than the outer or oxidized portion of the clay. This difference in the present instance is very great, amounting to many times as much sulphur. Hence, the amount of gaseous matter in the black portion of the ware being so much higher than in the red portion, it naturally follows that swelling is practically certain to develop first in the black areas.

We may say then, (a) that carbon is the beginning or first cause of the black-coring reaction, by preventing the timely oxidation of the sulphur and iron. (b) That iron is chiefly responsible for the black coloration, but only to a small degree accountable for the swelling, perhaps by assisting to hold the sulphur in the clay and perhaps in promoting the early fusion of the clay. (c) That sulphur is the final or actual cause of the swelling, chiefly by the substitution of silicic acid for sulphur.

When all three substances are present at once, they are joint agents, but sulphur is the worst, and most important cause. Clays high in carbon and iron but devoid of sulphur, would probably blacken by improper burning, but would not be likely to swell. Clays devoid of iron, but high in carbon and sulphur would probably swell, without blackening. Clays high in sulphur, and containing neither carbon nor iron, would still be likely to swell on over-fire, but on the exterior first instead of the interior.

The clearing up of the relative action of these three substances in the black-coring reaction, and the fastening of the harmful structural changes on the sulphur, rather than the stage of oxidation of the iron as was heretofore held, is the most important result of the investigation.

### *Blue-Stoning.*

II. The Blue-Stoning Reaction. Very little new matter has been brought out in this test on this subject. It does not

appear that there is any persistent or clearly marked change in the status of the iron during the darkening or blue-stoning reaction. The clay is a poor one in which to study this reaction, however, because of its short interval between vitrification and fusion, and because of the scoriaceous character of its fusion. So far as can be judged, then, Seger's theory of condensation is the most tenable ground upon which to explain blue-stoning for the present. The subject should be studied in other clays, low in sulphur and carbon.

### *Over-fire.*

III. This clay is not a good one for this subject, owing to its very short vitrification range. However, it indicates very clearly that the swelling of clays in fusion or by over-fire is almost exclusively a sulphur reaction. The gases evolved seem to be clearly traceable to the breaking down of sulphates, or their reduction by iron or carbon and the subsequent breaking down of the sulphites, or the replacement of sulphates and sulphides by silica. The latter reaction is probably the important one. Iron in itself is not shown to have any direct bearing on over-fire or on swelling. The swelling of black cores and of red portions are of one and the same nature, and the black swells first, merely because it contains much the most of the gas-forming matter, and possibly because fused earlier.

IV. The whole investigation emphasizes the importance of sulphur as the cause of a clay's defects in firing, far more than the carbon or the iron. It therefore points to the fact that sulphur should invariably be reported in a clay analysis, which is now rarely done. It also shows very clearly that the oxidation process, or that portion of the burn below 900°C, cannot be too carefully conducted—and that in sulphury clays, the period for slow steady roasting should be continued for hours after the carbon has all gone, and that even then, no matter how long we roast the clay, there will be enough sulphur still remain to easily swell it to a sponge if over-heated.

Therefore, for vitrified wares, the percentage of sulphur and carbon is the most critical point to be established by analytical means, and the selection of a clay low in any form of sulphur, is likely, all other things being equal, to give a wide vitrification range and a product of good physical strength.

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